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EVALUATION OF THE INTEGRATION OF THE SANDWELL CENTRAX$_{TM}$ PROCESS INTO AN INTEGRATED TWO-STAGE LIQUEFACTION PROCESS

PHASE I

FINAL REPORT

by

Sandwell Technologies

MICROMEDIA

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

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Reference: 23SQ.23440-4-9109
Evaluation of the Integration of the Sandwell Centrax Process into an Integrated Two-Stage Liquefaction Process - Phase I.

Dear Dr. Kelly:

Enclosed are (1) original and three (3) copies of the final report on the above referenced study. It describes the laboratory-scale development work of the Centrax process. Included are:

- analytical technique development,
- laboratory-scale experimental procedures and apparatus development,
- investigation of the effects of the independent process variables on the Centrax performance variables,
- multi-step separation/extraction simulations,
- simulation of different complete process arrangements including multiple separation and extraction and final extractant recovery,
- estimate of the Centrax process energy requirements with a comparison to potential liquefaction product recovery by application of the Centrax process principles.

.../2

This study shows that the process requirement of maximum ash separation combined with minimum liquefaction product loss is indeed a complex task. It involves the selection of the correct extractant(s) in combination with the application of the appropriate operating variables in each stage. Each stage, in turn, needs to be carried out in the correct order of processing.

CANMET support for Centrax development is very much appreciated and we look forward to discussing with you opportunities for further co-operation in the development of Centrax technology.

Yours very truly,

SANDWELL TECHNOLOGIES

P. G. Groeneweg

Dr. P.G. Groeneweg
Director, Technology Development

PGG:vb
cc. E.K. Fresque (title page and summary)

ACKNOWLEDGEMENTS

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Sandwell also acknowledges the co-operation of the Electric Power Research Institute in providing samples from the Wilsonville pilot plant and, in particular, we appreciate the efforts of Norman C. Stewart for his assistance and helpful technical commentary.

SUMMARY

This study was carried out to further the know-how of a previously conceived separation process for separating solid matter from hydrocarbon slurries. The process is called Centrax$_{TM}$, and as applied to coal liquefaction, it is a deashing process which separates oils, asphaltenes and pre-asphaltenes from ash and unconverted coal.

In the Centrax Process, solids are separated from the coal-derived liquids by displacing the non-distillable liquid fraction with a process-derived distillable hydrocarbon liquid (extractant). This extractant is then recoverd from the solids by flash evaporation. Extraction is achieved in multiple stages. All coal-derived liquids are kept in solution by the extractant so that at no stage in the process are the asphaltenes or pre-asphaltenes precipitated with the solids. This results in nearly complete recovery of all coal-derived material without solvent loss.

The specific objectives of this study were:

- to improve the experimental and analytical techniques on a laboratory-scale to make possible a more indepth study of the relevant process variables, and
- to investigate the effectiveness of the Centrax Process concepts as a product recovery/solids rejection system for the American Integrated Two-Stage Liquefaction process (ITSL) as operated at the Wilsonville Alabama 6 TPD pilot plant.

SOMMAIRE

Cet étude a été effectué au but de avancer les conaissances d'un procédé déjà concu pour séparation les matièrres solides d'un mélange des hydrocarbures. Le procédé est appele Centrax$_{TM}$, et il est applicable dans la liquefaction du charbon comme procédé d'enlèvement des cendres ("deashing process") pour séparer les cendres et le charbon nonréagi et en même temps récupérer quantitativement les huiles, les asphaltenes et les pre-asphaltenes.

Dans le Procédé Centrax, les solides sont séparés a partir des liquides dérivés du charbon par remplacant la fraction liquide non-distillable avec un liquide ("extractant") constitué des hydrocarbures distillables provenant de la liquefaction du charbon. Cet extractant est puis récupéré a partir des solides par évaporation. L'extraction est achevée dans une série d'étapes. Tout les liquides dérivés du charbon sont gardés en solution a l'aide de l'extractant de la mannière que auqun moment durant toutes les étapes du procédé ni les asphaltenes ni les pre-asphaltenes ne sont pas precipitées avec les solides. Comme résultat on obtient une récupération presque complete de tout les matières dérivées du charbon sans perte de solvent.

Les objectifs de cet étude furant:

- l'amélioration des téchniques expérimentales et analytiques a l'échelle de laboratoire pour permettre l' étude plus approfondi des variables critiques du procédé, et
- l' étude de l'éfficacité du procédé Centrax tel que concu pour la récupération de produits/rèjet des solides dans la cadre du procédé americain de liquefaction-du-charbon-a deux-étapes-integrées (ITSL) en operation a l'usine pilote de 6 tonnes par jour de Wilsonville en Alabama.

This study has been performed on samples from Wilsonville Runs 242 and 243 in the integrated two-stage liquefaction mode of operation. In Run 242, the coal slurry by-passed the thermal dissolver and therefore received only a short contact time reaction in the pre-heater. In the subsequent Run 243, the slurry flow from the preheater was passed to the thermal dissolver where it received on 25-50% of the normal reaction time. In both these cases, the coal was subjected to low severity initial processing. These test conditions therefore, represent a significant test of the Centrax Process feasibility.

Analysis of the samples received, showed evidence of product aging. It appears that the oils regressed into asphaltenes and the asphaltenes regressed into pre-asphaltenes. This factor also contributes to the potential degree of difficulty in separating the samples which were received. Fresh samples are probably easier to separate.

In spite of these conditions imposed on the tests, aged products from Wilsonville Runs 242 and 243 have been successfully recovered/separated by the Centrax Process. In particular, it was found that:

- Total liquid recovery by the Centrax Process is in the range of 98-99.5% for the samples. By comparison, deep vacuum evaporation results in recoveries of only 34.6-37.4% which in addition, produces a very hard, difficult to process non-friable residue with considerable THF soluble material trapped in the

Les travaux de cet étude ont été effectueés en utilisant des échantillons preléves durant les marches expérimentales 242 et 243 lorsque l'usine de Wilsonville opéra dans le mode de liquefaction a deux étapes intégrées. Durant la marche numero 242, le mélange d'alimentation (coal slurry) circonvennait le réacteur thermique de dissolution et par consequant recut un temps de réaction court dans la chaudièrre. Durant la marche 243, le mélange d'alimentation passait de la chaudièrre au réacteur thermique ou il recut seulement de 25 a 50% du temps normal de réaction. Dans ces deux cas, le charbon a été soumis a un traitement initial de basse sévérité. Est evident donc que, cettes conditions expérimentales représentent une épreuve sévére de l'applicablite et l'éfficacité du Procédé Centrax.

L'analyse des échantillons recus, présenta des indications de vieillisement des produits. Il appert que les huilles régressent vers asphaltenes et en même temps les asphaltenes régressent vers pre-asphaltenes. C'est probable que ce facteur contribua a la difficulté de séparation des échantillons recu. On croit que des échantillons frais seraient plus facile a séparér.

En dépit de conditions imposées sur les éssais par la qualitee des échantillons, la séparation/récupération des produits provenues de marches 242 et 243 de Wilsonville, par le Procédé Centrax a été une réussite. A la suite des ces travaux on a decouvert que:

- L'application du procédé Centrax pour la récupération du produit liquide dans les échantillons soumis a donne des résultats de 98-99.5%. Par comparaison, l'aide du vide avancé a comme résultat récupérations de 34.6% 37.4% ce en plus le residu obtenue est dur, non-friable, contenant beaucoup de matièrre soluble en THF captée dan la matrice solide, ce qui fait qu'il soit tres difficile a traiter.

- Ash concentrate obtained by the Centrax Process does not contain THF soluble materials and has good friable properties allowing for conventional and easy inter-transportation.

- One of the intermediate process streams, the separated solids cakes are very diffcult to handle due to their very viscous, 'sticky' plastic type of properties and need to be handled by specially designed mechanical equipment.

- Investigation of the different Centrax Process parameters showed that for these samples:

  - Ash concentrations of as low as zero can be achieved in the liquid product.

  - Ash removal efficiencies appear to be dependent on processing temperature, amount and type of extractant, centrifugal force and residence time.

  - Precipitation of asphaltenes and pre-asphaltenes appear to be dependent solely on type and amount of extractant and temperature.

  - There was no recovery of pre-asphaltenes and very little, if any, recovery of asphaltenes during the flash evaporation stage.

  - During the flash evaporation stage, gas and coke production can be minimized and needs further optimization.

  - The ash is separated from the process in a stream that is 100% THF insoluble.

- Le concentré des cendres obtenu en employant le procédé Centrax ne contient pas de matières solubles en THF et ses propriétés de friabilité sont bonnes, ce qui permettra le transport facile par des méthodes conventionnelles.

- Les croutes des solides séparés comme flux intermediare sont trés difficiles a manipuler a cause de leur propriétées plastiques, leur viscosité et adhérence et ils doivent être manipulées par les dispositifs mécaniques.

- L'investigation des differents paramétres du Procédé Centrax utilisant le échantillons fournis ont montré que:

  - La concentration de cendre dans le produit liquide peut être réduite jusqu'a niveaux de zero.

  - L'éfficacité de l'enlévement des cendres semble depeindre de la température d'opération, de la quantitée et le type d'extractant, du temps de résidence et force centrifuge.

  - La précipitation des asphaltenes et pre-asphaltenes semble depeindre uniquement du type et quantitée d'extractant et de la température.

  - Il n'y avait pas de pre-asphalténes et trés peu (ou pas du tout) de asphaltenes recuperées pendant l'étape de vaporisation instantanée.

  - Durant l'étape de vaporisation instantanée, la production de gas et coke peut être minimisée et exige une optimisation plus poussé.

  - Les cendres sont séparées sous forme d'un flux qui est 100% insoluble en THF.

Material balances have been calculated for two complete process calulations of the Centrax Process as applied to the Wilsonville pilot product recovery obtained in the bench-scale equipment are a reasonable expectation of the performance at a larger scale.

A convenient measure of the product recovery achieved by the Centrax deashing process stage is the amount of energy rejected in the ash concentrate expressed as a percentage of the energy in the feed coal to the entire coal liquefaction process. For Run 243, the energy rejection for the Wilsonville operation using the Critical Solvent Deashing (CSD) process for solids separation was reported to 20-26%. The process configurations proposed for an ITSL-Centrax process result in an energy rejection of between 10-13%. Since the residual energy rejected is in the form of unconverted coal, this means that essentially 100% of the coal liquids have been recovered.

The test results were achieved without any external solvents. Separation/recovery was carried out at atmospheric pressure and for these process materials at 180°C. As detailed above, the ash concentrate is a friable, non-sticky material which can be transported by conventional means.

By the appropriate selection of the process-derived Centrax extractant and the processing configuration, the energy requirement can be minimized. It is estimated that the Centrax

Les bilans des matièrres furent calculés pour deux simulations complétes du procédé Centrax tel que apliqué aux échantillons provenant de l'usine pilote de Wilsonville. La séparation et la récupération des produits obtenus a l'échelle de laboratoire représent une prevision raisonable de performance a l'échelle industriélle.

Un moyen comode d'éxprimer le niveau de récupération des produits achevé par le procédé Centrax est la quantitée d'énergie rejetée avec le concentré de cendre, exprimée en pourcentage de l'énergie contenu par le charbon introduit dans le procéssus de liquefaction entier. Pour la marche 243, l'énergie rejetée dans le cadre de l'opération de Wilsonville en employant le procédé de enlévement des cendres par extraction avec un solvent au conditions supércritiques (CSD) a été de 20 a 26%. Pour une configuratin du procédé comprenant ITSL-Centrax, l'énergie rejétée est seulement de 10 a 13%. En plus il faut considerer que l'énergie rejétée au cas de ITSL-Centrax est sous forme de charbon nonréagi ce qui signifie que essentiellement 100% des liquides dérivés du charbon ont été récupérés.

Les résultats expérimentales furent realisés sans employer auqun solvent externe. La séparation/récupération fut éffectuée a une préssion atmosphérique et une température qui pour ces produits fut de 180 degrées centigrades. Ainsi que on a décrit ci-dessus le concentré de cendre se présent comme une matièrre friable, pas du tout collante que pourra etre transportée par des moyens conventionnels.

Les demandes d'énergie pour ce procédé peuvent être minimisées par un choix approprié du éxtractant et de configuration du procédé. On estime que la demande d'énergie pour le procédé

Process energy requirement is about 1.4% of the heating value of the feed coal. Energy requirement for the Centrax Process is therefore expected to be comparable with the energy needs of competitive processes.

The Centrax process will probably not affect either the upstream or downstream ITSL process units. Instead, it may be possible to simplify the overall ITSL process by elimination of some of the ITSL process unit operations. For example, a vacuum distillation unit, which processes a mixture of heavy hydrocarbon liquids and solids, can be removed from the ITSL process. Separation is effected exclusively with extractants taken directly from process streams from the ITSL process without the requirement of preparatory processing.

In conclusion, the Centrax Process can be incorporated into integrated two-stage liquefaction processes as the solids separation/product recovery stage. Two process configurations have been developed and tested giving near complete recovery of liquefied coal product with minimum energy requirements.

The next stage of the work program will include on-going development of the process concepts, and development of a pilot plant scale continuous Centrax apparatus.

Centrax est de approx. 1.4% de la valeur calorifique du charbon alimenté. Donc de point de vue demande d'énergie on estime que le Procédé Centrax sera comparable aux autres procédé compétiteurs.

Il est probable que le Procédé Centrax ne affectera pas ni les étapes précédantes ni les étapes suivantes du procéssus de liquefaction-a-deux-étapes integrées (ITSL). Plutot, il serait possible de simplifier l'ensemble du procédé ITSL par l'élimination des quelques unités d'opération. Par exemple, l'unitée de distillation sous vide, impliquant le traitement de hydrocarbures lourdes en présence de matièrres solides, serrait eliminée du ITSL a la suite de l'introduction du Centrax. La séparation de solides est effectuée au cas de Centrax exclusivement a l'aide des extractants obtenus diréctement a partir des intermediaires du procéde ITSL sans besoin de préparation additionnéle.

En conclusion, le procédé Centrax peut être incorporé dans tout les procédés de liquefaction a deux étapes integrées pour récupérér les produits liquides et enlèver les solides. Deux configuration de procédé ont été dévèlopées et expérimentées, toutes les deux donnant une récupération presque totale du produit de liquefaction avec demande d'énergie minime.

La phase suivante de ce programme de travail incluera la continuation du développement des concepts du procédé et le développement d'un apparail Centrax a l'action continue a l'échelle pilote.

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1.0 INTRODUCTION

1.1 Centrax Separation - Process Description

The Centrax process is an innovative technology for the complete separation of solids from mixtures of liquid hydrocarbons. The process is particularly well-suited to the removal of ash and unconverted coal from the products of coal liquefaction. It is well-known that coal liquefaction products are mixtures of oils, asphaltenes and pre-asphaltenes and that the separation of solids from asphaltenes and pre-asphaltenes is particularly difficult.

Since asphaltenes and pre-asphaltenes by their nature cannot be separated by distillation, other techniques must be used to recover these materials from ash and unconverted coal. Advanced processes such as Critical Solvent Deashing and Anti-Solvent Deashing precipitate a portion of the pre-asphaltene fraction to improve the rate of gravity separation of solids; however, at the expense of loss of these hydrocarbon fractions.

In the Centrax process, both complete product recovery and solids separation is accomplished by the displacement of all liquid hydrocarbons, including the oils, asphaltenes and pre-asphaltenes from the solids using a specially selected process-derived extractant which is recoverable by evaporation and which is soluble with the oils, asphaltenes and pre-asphaltenes throughout all process steps.

The process is carried out in specially designed equipment to achieve efficient and effective extraction, separation and extractant recovery.

In the first stage, the insoluble solids (ash and unconverted coal) are separated from the solution formed by the addition of the extractant by the application of centrifugal forces to produce a clear centrate and a compacted solids phase with minimal residual liquid hydrocarbons.

In subsequent stages the residual asphaltenes and pre-asphaltenes in the compacted solids phase are separated by the further addition of an extractant, followed by centrifugal separation to form a solids phase from which the asphaltenes and pre-asphaltenes have been extracted and displaced by the process-derived extractant.

In the final stage, the volatile extractant is recovered from the interstitial spaces of the solids cake, yielding a dry and friable ash concentrate.

The above is a generic description of the process which can be tailored to suit any combination by solids and liquid hydrocarbon mixtures to effect complete product recovery and solids recovery. Product factors that can be varied include:

- source and quantity of extractant

- number of stages

- cross-, counter-, or co-current processing configurations

- separation conditions (e.g. temperature, G-force, residence time etc.)

The Centrax process is a very flexible and versatile method for deashing, capable of processing coal liquefaction products containing both low and high levels of asphaltenes and pre-asphaltenes. As such, the Centrax process can be employed in liquefaction processes directed to the production of a mixed product slate as well as all distillate products. In other words, the Centrax deashing step can be employed as an inter-stage deashing step or as a final dashing step.

Moreover, there is no reason to expect that Centrax deashing will not be equally effective in separating solids resulting from the liquefaction of a wide range of coals including lignite, sub-bituminous coals and the bituminous coals which are the subject of considerable research and development in the United States and Great Britain.

The following section considers the prospects and applicability of further development of the Centrax process in conjunction with pilot coal liquefaction plants operated or planned in other countries.

2.0 OPPORTUNITIES FOR CENTRAX DEMONSTRATION AND COMMERCIALIZATION

The absence of a pilot scale coal liquefaction facility in Canada represents a major obstacle to the liquefaction process. Many countries have found that the construction of pilot plants capable of processing several tons per day of coal are essential to the timely development of alternative energy processses. Such plants fulfill important functions, namely:

- acquisition of valuable hands-on processing experience at sufficient scale to appreciate significant operating difficulties.
- integrated recycle operation to test the ability of the process to generate adequate quantities of recycle solvent with the appropriate solvent and H-donor properties.
- generation of stocks of products for related bench-scale research into such topics as:
    - product upgrading studies
    - environmental and pollution control studies
    - product inspection
    - product separation studies.

Canadian process developers at a stage of technological development beyond the scale of bench units must gain access to foreign pilot plants to secure a supply of samples for on-going development in Canada or to participate on-site if integrated operation is required. Such a situation exists for the further development of the Centrax deashing process, which dictated an investigation into the prospects and opportunities to advance the Centrax deashing process in connection with government sponsored projects in the U.S. and United Kingdom.

This next section reviews the status and nature of joint development opportunities in those countries and the justification for the final decision to attempt to link Centrax with the Wilsonville, Alabama pilot plant co-sponsored by the U.S. Department of Energy and the Electric Power Research Institute.

2.1 Point-of-Ayr Liquid Solvent Extraction (LSE) Pilot Plant

The coal liquefaction development in the U.K. has been carried out by the National Coal Board (NCB) with financial support from the Department of Energy. The current direction being taken in the U.K. is to pilot the liquid solvent extraction (LSE) process which has been developed for British hard coals with less than 10% ash. The process is essentially a two-stage liquefaction process with inter-stage deashing by filtration. The process is characterized by the low pressures used in the first stage of the process.

The following more fully describes the process as reported by Thurlow(1):

> "A flow sheet for one typical configuration of the process is shown in Figure 1 (Appendix 3). The coal is crushed, dried and then

slurried with the recycle solvent oil. The slurry is rapidly heated to about 400°C and fed to a digesting reactor which operates at less than 20 bar. A high level of extraction (up to 95% of the coal substance) can be obtained, the solvent acting as a mild hydrogen donor such that the hydrogen content of the extract has increased typically about two percentage points. The resulting digest is then cooled and passed to a gas/liquid separation vessel before the slurry passes to the filter unit.

Batch filtration, using commercially developed leaf or candle filters, are used. The relatively low pressures employed and the fact that digestion conditions can be optimized to give fast filtration rates have confirmed our belief that this is a perfectly viable engineering process. The final filter residue is, in the design shown, transferred to a gasifier, though alternative configurations are considered later. Further coal, as necessary, is fed to the gasifier which can be of a number of designs, but is likely to be pressurized and oxygen-blown.

The filtered liquid, after adjustment of the extract concentration is then fed to the hydrocracker unit where it is mixed with hydrogen rich gas at high pressure (of the order of 200 bar) and heated to the feed temperature. Further hydrogen is used as quench gas to the hydrocracker. The process used is conventional hydrocracking wherein excess hydrogen is reacted catalytically at high temperature and pressure with the coal extract. A large number of catalysts, both commercial and novel, have been tested, and the evidence is that a catalyst life of at least 4,000 h should be achieved before it has to be changed. The product from the hydrocracker is cooled and separated into gases and liquids in a multi-stage flash separation system to give the required products, boiling below typically 275°C, the higher boiling point fraction being recycled or taken out as pitch."

The Centrax process could be integrated into an LSE type process. This would be achieved by replacing the filtration step by the Centrax process.

The filterable solids resulting from the first stage LSE liquefaction would probably be separable by the application of centrifugal force as required by the Centrax process. Product recovery would be equal or better than that achieved by single-stage filtration and could be accomplished in less time with smaller scale equipment.

At present, the facilities at the Coal Research Establishment (CRE) of the NCB at Stoke Orchard, Cheltenham, are inadequately sized to provide streams for Centrax deashing development let alone integrated process development of the LSE process.

Plans are underway to design a 2.5 TPD pilot plant to be built at Point-of-Ayr in Wales. Although such a plant would appear to offer a

needed scale-up for the LSE process it is not likely to provide any opportunity for the development and demonstration of Centrax technology over the next several years. The plant will not be operating for several more years. Furthermore, there appears to be a very strong desire to operate with British coals and technology during the initial years thus limiting Canadian development opportunities unless large upfront investments were made to participate in the plant.

Almost of equal importance is the need to have access to proven pilot facilities with excellent operability, a background of operating performance data in various operating modes, large stocks of products and proven mass balances. None of these will exist until several years of operation has been accomplished at Point-of-Ayr.

Although technically feasible, the integration of Centrax technology into the LSE process would not appear to offer the required timely development opportunity.

2.2 Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama

At the present time the only operating coal liquefaction pilot plant in North America is situated at Wilsonville, Alabama. This facility was originally designed as a nominal 6 TPD solvent refined coal (SRC) pilot plant. Operation with coal began in January 1974 and since then has operated for significant periods every year. The facility has been continuously upgraded with the addition of a Critical Solvent Deashing unit for solids separation and a hydrotreatment unit based on H-Oil technology. A flow diagram of the pilot plant can be found in Appendix 2.

The Advanced Coal Liquefaction R & D facility at Wilsonville is funded by the U.S. Deparatment of Energy (DOE) and the Electric Power Research Institute (EPRI). Southern Company Services, Inc. (SCS), manages the Wilsonville program on behalf of the DOE and EPRI, while Catalytic, Inc., operates the facility under subcontract with SCS.

During 1983 and the first half of 1984, the facility was operated in Integrated Two-Stage Liquefaction (ITSL) mode using Illinois #6 coal. The facility at Wilsonville is exceedingly well-managed with complete and informative technical progress reports prepared on each run.

These reports contain information on the following aspects of the pilot plant operation and performance:

- system stability,
- performance evaluation for the individual SRC, CSD, and HTR units,
- properties and inspections on distillate products, recycle and process solvents,
- characteristics of residual products,
- mass balances over steady-state periods,

- maintenance problems,
- catalyst activity,
- corrosion measurements,
- environmental protections.

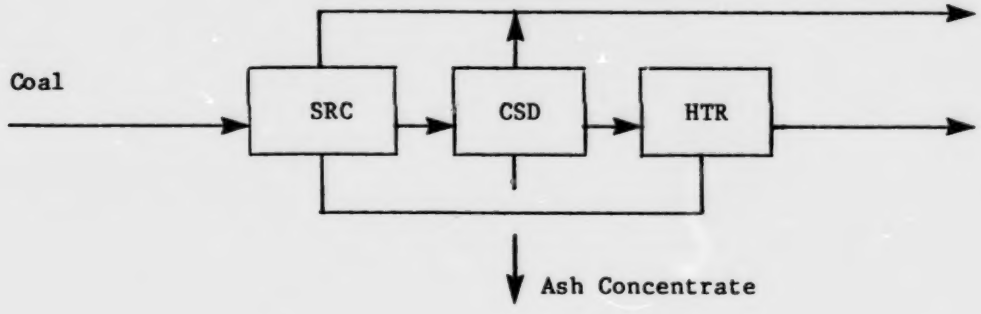
In short, the extensive monitoring activities, complete reports and the availability of samples makes the Wilsonville facility an ideal location, as well as the only one, for undertaking process development work on technologies that must be integrated successfully into both upstream and downstream hydroprocessing unit operations. Since major coal liquefaction innovations in the United States sponsored by the USDOE and EPRI must be piloted at Wilsonville to be proven feasible both technically, and economically, the ultmate process configuration established at Wilsonville will likely represent the basis for the commercial coal liquefaction synfuels business in the United States.

As a result of this determination that the development of the Centrax process could be best pursued with access to Wilsonville materials and eventually an on-site demonstration at Wilsonville, an effort was made to obtain the assistance and co-operation of EPRI. The initial assessment by EPRI is that the process concepts are workable and attractive in terms of product recovery and stabilty. More information would be required on the economics of the process but that would be dependent on a specific process configuration for an integration into the two-stage liquefaction process at Wilsonville using products produced from American bituminous coals. In order to assist Sandwell in the further assessment of the prospects for Centrax integration, EPRI made a commitment to supply samples of process streams from Wilsonville for use in the investigation. To generate in Canada the quantities of product received from Wilsonville, would have cost several hundred thousand dollars. To obtain like materials in a timely way with all the attendent background data would have been otherwise impossible.

The co-operation of EPRI has made possible the execution of the work in the sections to follow and represents a major contribution to the project, the value of which should not be underestimated.

2.3 Considerations in the Development of Centrax Deashing with Wilsonville Materials

The Wilsonville pilot plant was operating in an Integrated Two-Stage Liquefaction (ITSL) mode with Illinois #6 coal at the time samples were provided for the evaluation of Centrax Deashing. The following illustrates the general arrangement between the Solvent Refined Coal (SRC), Critical Solvent Deashing (CSD) and Hydrotreater Units (HTR) in operation at Wilsonville.



In evaluating the Centrax Deashing process as a possible replacement of the CSD process, it was necessary to decide initially how Centrax could be integrated into the ITSL mode of operation. The direct substitution of the Centrax process in place of the CSD arrangement does not permit the full benefit of Centrax Deashing to be realized since distillates which need not be removed for use in the Centrax process, are partially removed prior to processing in the CSD units. In other words, whereas concentration of the heavy hydrocarbons (asphaltenes and pre-asphaltenes) is desirable prior to the critical solvent separations, this is not true for the Centrax process. Keeping the asphaltenes and pre-asphaltenes diluted is not a disadvantage in the Centrax process. Therefore, the Centrax process was evaluated for Wilsonville ITSL mode using as a feed material a process stream with greater flow and upstream to that employed in CSD processing. The feed stream selected was the bottoms of vessel V110 which is the low pressure flash tank following the SRC dissolver. The location of these units are shown in Appendix 2.

Throughout this report, reference is made to the feed material used in the Centrax evaluations as V110 BTM which is the description given to this stream at Wilsonville. The stream contains the dissolved coal fractions, recylcle solvents, undissolved coal and ash, minus the light fraction flashed off in the high and low pressure separators.

Another difference between the CSD process and the Centrax process is in the use of deashing solvents. The CSD process uses an external proprietary solvent, whereas the Centrax process employs a process-derived extractant. Therefore, it was also necessary to select a process stream having the appropriate extractant properties. The stream selected, and used in most separation tests, was the bottoms from the T105 distillation unit located in the HTR section of the plant. This material is also used as the hydrotreated solvent in the SRC unit. It is a mid-to heavy distillate material and is coal-derived. Other extractants which were employed in this study were, for example, cuts of V110 feed material.

The samples used in this study came from two runs at Wilsonville in the ITSL mode. In run 242, the coal slurry by-passed the thermal dissolver

and therefore received only a short contact time reaction in the preheater. In the subsequent run, Run 243, the slurry flow from the preheater was passed to the thermal dissolver where it received only 25 - 50% of the normal reaction time. In both of these cases, the coal was subjected to low severity initial processing. These test conditions therefore, represent a significant test of the Centrax process feasibility. The samples used in the test program are identified as either a process stream from run 243 or 242. In general, most of the work was conducted on run 243 materials.

3.0 ANALYTICAL AND EXPERIMENTAL PROCEDURE DEVELOPMENT

In undertaking an evaluation of the feasibility of integrating the Centrax process into the ITSL liquefaction arrangement, it is necessary to employ rigorous analytical and experimental procedures. Several factors have made this of particular importance, namely:

- the small quantities of materials being processed,
- the relatively large random experimental errors, and
- the aging of materials.

Accordingly, prior to establishing the analytical and experimental protocol as described in Section 5.1, considerable development effort went into ensuring the accuracy and repeatability of the testing procedures used in the study. In this section, the problems and the resultant techniques used are discussed with respect to both analytical procedures and experimental technique. As a result of these efforts, the evaluation of the integration of Centrax Deashing into ITSL liquefaction is based on solid methodology and analytical accuracy. The following description of the steps taken to establish sound experimental protocols also provides a useful insight into the practical aspects of deashing coal liquids at any scale.

3.1 Analytical Technique Development

The areas where analytical technique refinement and development was required are as follows:

- sampling technique
- sample preparation
- filter media selection
- ash determination

3.1.1 Sampling Technique

The sub-sampling of raw materials containing solids posed several problems. The materials had segregated with solids settling to the bottom. This was due to storage. In addition, these materials were extremely viscous, virtually solid at room temperature. These undesirable characteristics were neutralized by heating the entire sample to make it less viscous and mixing vigorously prior to sub-sampling into smaller, more workable portions, by the process of flaking and grinding.

The light material required a much simpler procedure such that stirring was found to be sufficient to create a homogeneous sample.

Sampling of product streams after processing posed additional problems. The compacted solids phase was small and heterogenous in nature, both in the radial and axial direction. These difficulties were overcome by using the entire stream for samples and sampling by taking a cross sectional wedge. The separated liquid is non-viscous and homogeneous at processing temperature but is viscous and non-homogeneous after it is allowed to cool. Sampling is conducted by decanting the separated liquid into sample beakers immediately after processing. This ensures homogenity and negates the requirements to reheat and remix the decanted portion to sub-sample it.

The procedures developed for sub-sampling ensure the homogeneity of samples required to evaluate the performance of the separation/extraction procedure.

3.1.2 Sample Preparation for Asphaltene, Pre-Asphaltene and Solids Determination

Determination of oil, asphaltenes, pre-asphaltenes and solids are accomplished by solvent extraction and insoluble collection, utilizing THF, toluene and hexane as solvents. In order to achieve accurate and repeatable results, the preparation of the sample is vital. It is essential to maximize solvent/sample contact.

The initial method of sample preparation for analytical determinations consisted of the following steps:

1. To approximately a 1 gram sample

2. Add appropriate solvent

3. Warm in a water bath for 1/2 hour stirring occasionally with a glass rod,

3. Cool sample to room temperature.

This technique was found to be unreliable primarily because the solids precipitated out and settled on the bottom of the beaker. This limited the exposure of the sample to the solvent which is needed in order to extract the soluble portion . This was especially prevalent in the hexane insoluble analysis. Since hexane is a relatively weak solvent, the dispersion of the solids were insufficient to allow for a complete dissolution of the soluble fraction.

In order to increase the dispersion of the hexane insolubles, a small amount of a stronger solvent was used in a few tests to break up the solids in the initial sample. An excess amount of hexane was added to precipitate the hexane insolubles and the rest of the procedure was as outlined previously.

Hence, the need to maximize the solids dispersion and solvent extraction led to the development of the procedure as outlined in Section 5.3.

The advantages of this method are:

- The heating of the sample to make it more fluid maximizes sample/solvent contact when the solvent is added.
- Constant stirring keeps the solids in suspension and maximizes sample/solvent contact.
- Constant heating increases the dissolution of soluble compounds and maximizes solids dispersion since solubility is a function of temperature. When the sample is cooled to room temperature, the extra compounds in solution due strictly to the elevated temperature will percipitate out.

3.1.3 Filter Media Selection

Insoluble fractions in the samples are collected by vacuum filtration. Throughout the course of the research, three different types of filters were used. These were: glass fibre (Whatman 934H), cellulose (Whatman 42) and polyvinylidene diflouride membrane (Millipore Duropore).

Initially, glass fibre circles were used but were deemed unsatisfactory as it was found that some of the smaller particles were not collected. This is primarily a problem in THF insoluble collection, especially in the separated liquid where the solids are characteristically small. These smaller particles must be collected in order to quantify solids removal performance.

These filters also had as an added complication. They had a tendency to absorb atmospheric moisture. Through the rigorous use of a desiccator in cooling and weighing the oven dried filters, moisture absorption effects were minimized.

The performance of the membrane filters was found to be advantageous as the moisture problem was eliminated. Furthermore, the pore size was such that all the insolubles were collected. As shown in Table 3.1, considerable additional solids were collected on Duropore filters from the filtrate of various filtrations conducted with glass fibre and cellulose filters. Addition of these solids to those collected by the other filters yielded comparable results to those obtained when Duropore filters were used for the entire sample.

Durpore filters cannot be ashed, hence ash determinations were performed on the hexane insolubles collected by a Whatman 42 filter. It is believed that the problem of small particles passing through the filter, as described earlier, is non-existent since the asphaltenes and pre-asphaltenes co-precipitate with the solids and form a larger precipitate.

TABLE 3.1 EFFECT OF FILTER TYPE ON THE THF SOLIDS DETERMINATION

	One Whatman 934H	Two Whatman 934H	One Whatman 42	One Duropore 0.22 µm
1) % THF solids collected	1.69,1.68*	1.65,1.57	NA	2.56,3.19
2) % solids collected from filtrate by Duropore 0.22 µm	1.20,1.54	1.46,1.75	1.30,1.41	NA
Total solids (sum of 1 & 2)	2.89,3.22	3.11,3.32	NA	2.56,3.19

* Second numbers are repeat determinations.

3.1.4 Ash Determination Technique Development

An evaluation of the ash determination was performed. The results are summarized in Table 3.2. The investigation consisted of using the THF insoluble fractions of the three major types of streams encountered in this research: feed material ($\sim$ 5% ash) compacted solids (>10% ash) and first stage separated solids (<1% ash) and igniting them at 925°C for different periods of time. In addition, toluene and hexane insolubles of the starting material were also ashed.

Results show that as the time increases the % residue decreases until a minimum is reached at 1-2 hours. After this point the % ash increases. This is probably due to metals in the ash that are being oxidized when exposed to these elevated temperatures.

Comparison of results using the toluene and hexane insoluble show that the % Ash is within 5% of those determined by THF insolubles at an elapsed time of 1-2 hours.

Based on this investigation the procedure for ash determination consisted of igniting the THF, toluene and/or hexane insolubles at 925°C for a period of 1 hour as per Section 5.1.3.

3.2 Experimental Procedure Development

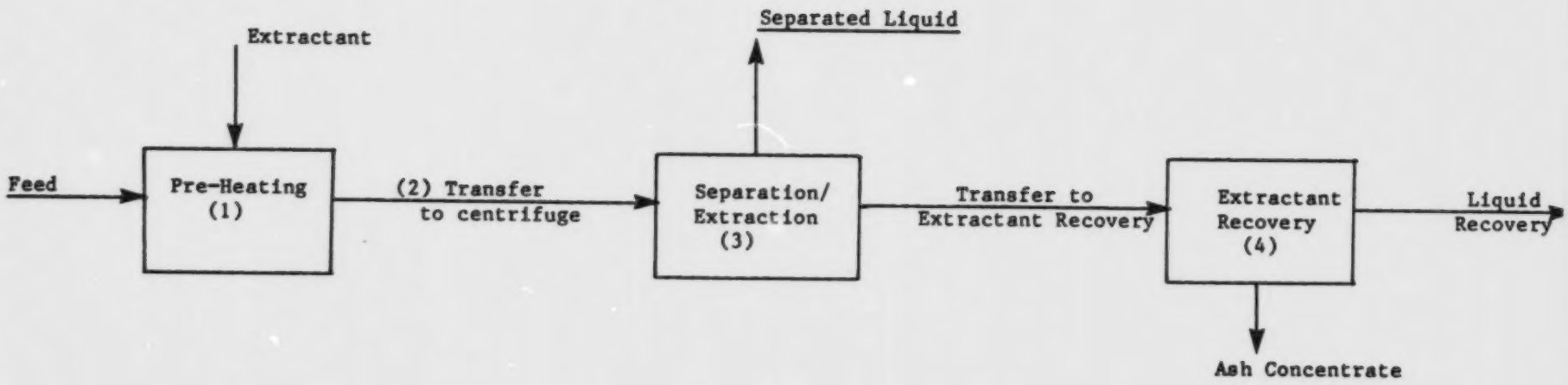
The Centrax process involves several distinctive steps which need to be performed in the laboratory at a small-scale in a manner which will reproduce as closely as possible likely conditions at larger scale. It is, of course, equally important to be able to repeat results performed at the bench-scale. In the Centrax process, there are four operations that have to be performed sequentially in the laboratory as batch operations at bench-scale and are parallel to steps in a continuous Centrax process.

These are shown schematically in Figure 3.1.

TABLE 3.2 EFFECT OF TIME ON % ASH DETERMINATION OF PROCESS STREAMS BY COMBUSTION AT 925°C

ELAPSED TIME (MIN) \ SAMPLE	Experiment 30 (% Ash)					Experiment 40 (% Ash)		
	Feed			Separated Liquid	Compacted Solids	Feed	Separated Liquid	Compacted Solids
	THF Insolubles	toluene Insolubles	hexane Insolubles	THF Insolubles	THF Insolubles	THF Insolubles	THF Insolubles	THF Insolubles
5	10.68	23.87	37.74	7.55	23.51	15.56	10.72	24.68
15	4.32	16.04	25.81	0.35	14.79	6.24	6.36	13.00
30	4.42	10.03	13.33	0.48	13.06	6.43	4.82	11.50
60	4.52	4.73	4.55	0.58	13.10	6.54	4.84	11.65
120	4.50	4.66	4.48	0.45	13.06	6.33	4.80	11.67
180	4.58	4.81	4.68	0.57	13.15	6.60	4.84	11.69
240	4.51	4.67	4.57	0.54	13.06	6.43	4.77	11.58
600	4.63	4.74	4.46	0.57	13.14	6.43	4.76	11.71

FIG. 3.1 LABORATORY-SCALE PROCESS SIMULATION



( ) denotes experiment procedure

The following section discusses the specific difficulties and techniques developed to maintain control over operating parameters such as, temperature and force of separation. In addition, special equipment was required to simulate the separation/extraction and extractant recovery stages. A description of the final experimental procedure is provided in Section 5.2.

3.2.1 Pre-Heating

During the pre-heating step, the mixture of feed and extractant is preheated and mixed. The procedure development was centered on the refinement of the mixing procedure and the utilization of a suitable container for the mixture. The sample is manually mixed throughout the preparation stage using the paddle end of a spatula. This is done to keep the solids in suspension and to maximize feed and extractant contact. At the end of the procedure the mixer had to be removed but it was found that certain components would preferentially adhere to it. These are believed to be asphaltenes and pre-asphaltenes as determined by means of mass balances. The end of the spatula was scraped and this material was allowed to drop back into to mixture. The spatula was weighed afterwards to correct material losses. This level of care is required by the small samples handled. This procedure, installed early into the testing program, assures the homogeneity of the sample in this processing step.

The use of the tube was discontinued and a centrifuge shield was used in its place. A shield is normally used together with a tube, where the tube is placed inside the shield and acts as a holder. The shield was used alone for two reasons:

- larger volume of material could be processed
- wider opening available for mixing purposes

3.2.2 Transfer

Since the mixture is heated to an elevated temperature, heat losses during transfer of the sample from the oil bath to the centrifuge can be appreciable and must be minimized. Temperature control is important at this stage because any heat losses occurring here will have to be recovered during the separation stage which will complicate the determination of the temperature profile during the subsequent separation processing step.

Minimizing heat losses was accomplished by using the same container for the preparation and separation/extraction stage and using an insulated glove to handle it during this procedure.

To compensate for the inevitable heat losses during the early stages of the experimentation program, the mixture was heated approximately $10^{\circ}C$ above the prescribed temperature. As the transfer mechanics became more streamlined and efficient, this practice was discontinued.

3.2.3 Separation

The separation step development was centered in the areas of temperature control and the mechanical adaptation of the centrifuge to the needs of the experimentation.

The centrifuge employed was a modified clinical type with a 4 place horizontal head and a maximum speed of 3200 rpm. The speed was monitored periodically throughout the course of the work using a tachometer.

Operation at temperatures higher than those for which the centrifuge was designed necessitated certain modifications and precautions. These included the installation of a cooling system for the electric motor consisting of nitrogen blown into the motor and water-cooled coils encircling the outside of the motor housing. The procedure adaptation included frequently greasing the bearing with a suitable high temperature lubricant and the construction of a fiberglass jacket to insulate the bowl and lid.

Heating of the centrifuge was accomplished by blowing hot air into the bowl of the centrifuge. A thermocouple was placed inside the bowl to monitor separation/extraction temperature. The centrifuge was preheated to a temperature approximately 40^{o}C higher than required to compensate for start-up heat losses. These occur during transfer of the shield and during start-up of the centrifuge when the spinning action of the head acts like a fan and draws hot air out of the bowl.

During separation, the temperature was maintained by blowing additional hot air into the bowl. Through the use of an adequate flow of hot air and well-placed insulation, the temperature was kept at the desired value throughout the duration of the separation procedure.

The above procedures and equipment modifications ensures that separation force and temperature were well controlled.

3.2.4 Extractant Recovery - Vacuum Evaporation

Initially vacuum evaporation was to be used to recover the liquids from the compacted solids. The evaporation was performed as outlined in Section 5.2.

The evaporation was performed at 20 mmHg. This pressure was chosen to simulate a typical industrial application. The evaporation was continued until cracking occurred as evident by white vapours in the receiver.

3.2.5 Extractant Recovery - Flash Evaporation

The experimental procedure simulating flash evaporation underwent considerable development throughout the course of the experimental program. This development was centered in four areas; the improvement of the evaporator through three prototypes and the improvement in the method of introducing the sample into the unit and the determinations of the ideal temperature and plate angle.

The unit evolved from an inclined plate with a vacuum hood to collect the vapours, to an enclosed unit where the vapours are swept away by nitrogen gas and finally to a tightly sealed nitrogen swept unit complete with a stand such that the unit can be inclined to any desired angle.

The inclined plate with vacuum hood was used primarily to facilitate flash recovery of the liquids. The small vacuum used for the collection of vapours was found to be unsuitable for this type of operation as the system could not handle the volume of vapours produced. The solution was found by using a sealed unit with nitrogen available to sweep away the vapours and downstream condensers to recover the oils. This proved to be an adequate way of capturing the volatiles. This also eliminated the fire potential presented by air being drawn into the evaporation chamber. The third unit was designed and built to reduce the frequency of leaks to which the second unit was susceptable.

Initially, the mode of sample introduction into the unit consisted of the following procedure. Firstly, in order to make it more fluid, the sample was diluted with oil to a composition of approximately 30% THF insolubles. Secondly, it was warmed, making it very fluid before introduction into the evaporator. When the second unit was used, a different method had to be employed. An injection type method was chosen using a pusher to inject the sample into the unit. Various nozzles were constructed in order to direct and spray the slurry onto the plate. Generally these were found to be unsuitable as they tended to be plugged by the solid particles and too much material stayed behind in the injector. The final injection system consisted of a straight open stainless steel tube fitted with a hand operated piston pusher. The injector was sealed through the use of a "viton" O-ring to prevent vapours from escaping past the piston. The end of the pusher was designed to go past the end of the tube so that all the sample would be injected into the unit. For this injection apparatus no dilution of sample is required.

The plate angle is an important consideration in the performance of the unit. The ideal situation is one that will result in the ash concentrate evenly spread in a thin layer over the length of the plate. This will minimize residence time and maximize evaporation. This angle is a function of the physical characteristics of the feed

(i.e., composition, viscosity) and operating conditions of the unit i.e., mass flow rate of feed, temperature. Proper angles were determined through trial runs and visual observations.

Plate temperature is an equally important consideration. The temperature must be high enough to evaporate all the oils including the higher boiling point fraction ($500^{\circ}C+$). However, the temperatures in excess of those required will promote thermal cracking of the liquid and production of gases such as, methane and ethane. These gases are undesirable products and must be minimized. The measured value of temperature is not the actual temperature at the evaporation surface since the location of the thermocouple is some distance away so as not to interfere with the formation of the ash concentrate. The optimum temperature was determined by means of mass balances to determine liquid recoveries and establish if non-condensible gases were formed and analysis of the ash concentrate to ascertain if THF soluble material remains.

3.2.6 Extractant Recovery - Vacuum Evaporation Versus Flash Evaporation

The decision to proceed with flash evaporation was based on a direct comparison of results from typical vacuum and flash evaporations.

These results are summarized in Tables 3.3 and 3.4 respectively for conditions as noted.

The results for vacuum evaporation indicate that all of the oils were recovered and there is no recovery of asphaltenes and pre-asphaltenes. This is as expected since asphaltenes and pre-asphaltenes are considered non-distillable. The fact that the evaporation bottoms are 100% THF insoluble tends to indicate that the asphaltenes and pre-asphaltenes were degraded into THF solids. The residue was a black, hard, non-friable solid.

In the case of flash evaporation, the most outstanding results seem to be that not only was all the oil recovered but a large portion of the asphaltenes and pre-asphaltenes have been converted into hexane soluble material as well. The residue is 100% THF insoluble and its physical characteristics were those of a porous, friable, greyish-black solid. As a result, it was decided to proceed with flash evaporation as the mode of extractant recovery based on the following conclusions:

- Flash evaporation could be carried out at atmospheric pressure.
- Flash evaporation resulted in an ash concentrate that was easier to handle.

TABLE 3.3 EXTRACTANT RECOVERY BY VACUUM EVAPORATION AT 20 mm Hg.

Total (wt %) / Components (wt %)	FEED*	PRODUCTS	
		Overhead	Residue
	100	53.6	46.4
O	51.7	53.6	-
A	6.4	-	-
PA		-	-
UC	20.5	-	20.6
Ash	22.7	-	25.8

* V110 BTM 243 and T105 BTM 243 (1:0.2) and three successive separation/extractions with equal amounts of T105 BTM 243.

TABLE 3.4 EXAMPLE OF EXTRACTANT RECOVERY BY FLASH EVAPORATION AT ATMOSPHERIC PRESSURE

Total (wt %) / Components (wt %)	FEED	PRODUCTS	
		Overhead	Residue
	100	48.16	51.82
O	36.9	47.23	-
A	13.2	0.93	-
PA			-
UC	23.9	0	25.9
Ash	26.0	0	26.0

* V110 BTM 243 and T105 BTM 243 (1:0.1) and one additional separation/exraction with equal amounts of T105 BTM 243.

4.0 ACCURACY AND REPRODUCIBILITY OF MEASUREMENTS

4.1 Analytical Precision

Throughout the course of the experimental program numerous analyses were performed on the feed material samples - V110 BTM 243 and V110 BTM 242. These were conducted in order to monitor the composition of raw materials during the research instead of relying on only a few analysis. The analyses can be used to establish a statistical evaluation of the analytical techniques.

Figures 4.1 and 4.2. show the variations over time in these results for hexane, toluene and THF insolubles and ash performed throughout the research program.

No obvious trends as a function of time appear in the data with respect to hexane and toluene insolubles and ash. Some random scatter is evident for all analyses with the hexane insolubles analysis exhibiting the largest scatter. The ash determination showed the least variability.

In contrast, a trend of increasing THF insoluble material is evident over the 8 months of experimentation, as shown in Figure 4.1. This tends to indicate that some retrogression of liquids to THF solids is taking place. This is fully discussed in Section 4.2.

Confidence levels of 95% were used to statistically evaluate the results which are summarized in Tables 4.1 and 4.2 for V110 BTM 243 and V110 BTM 242 respectively.

TABLE 4.1 V110 BTM 243 - REPEAT ANALYSIS

Insolubles	#of Analyses	Mean wt %	95% Confidence Range wt %	Standard Deviation
hexane	46	53.80	51.68 - 55.92	7.04
toluene	43	24.03	22.72 - 25.35	4.39
THF	46	9.65	9.23 - 10.06	1.43
Ash	33	4.53	4.44 - 4.62	0.26

FIG. 4.1 V110 BTM 243 COMPOSITION

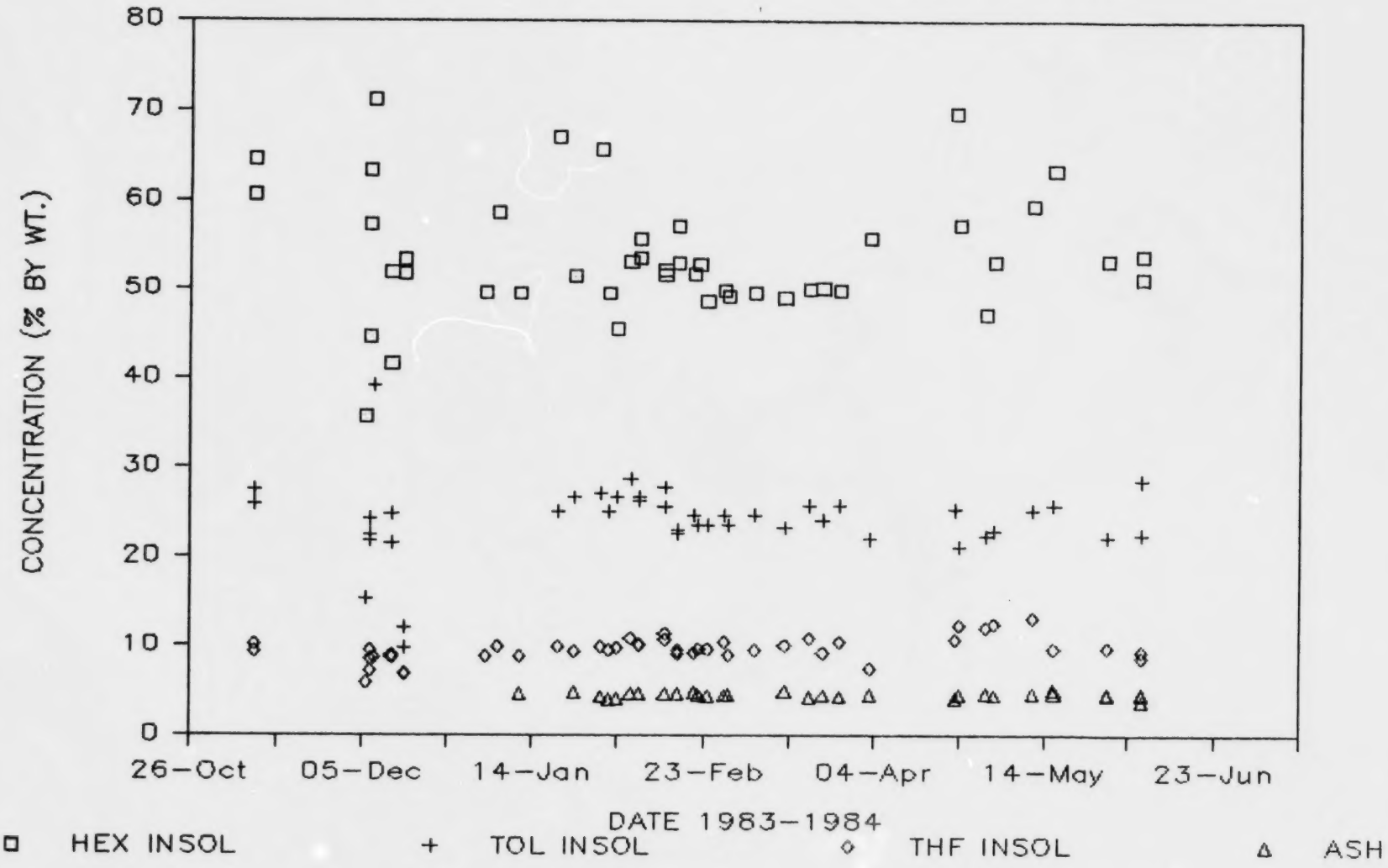


FIG. 4.2 V110 BTM 242 COMPOSITION

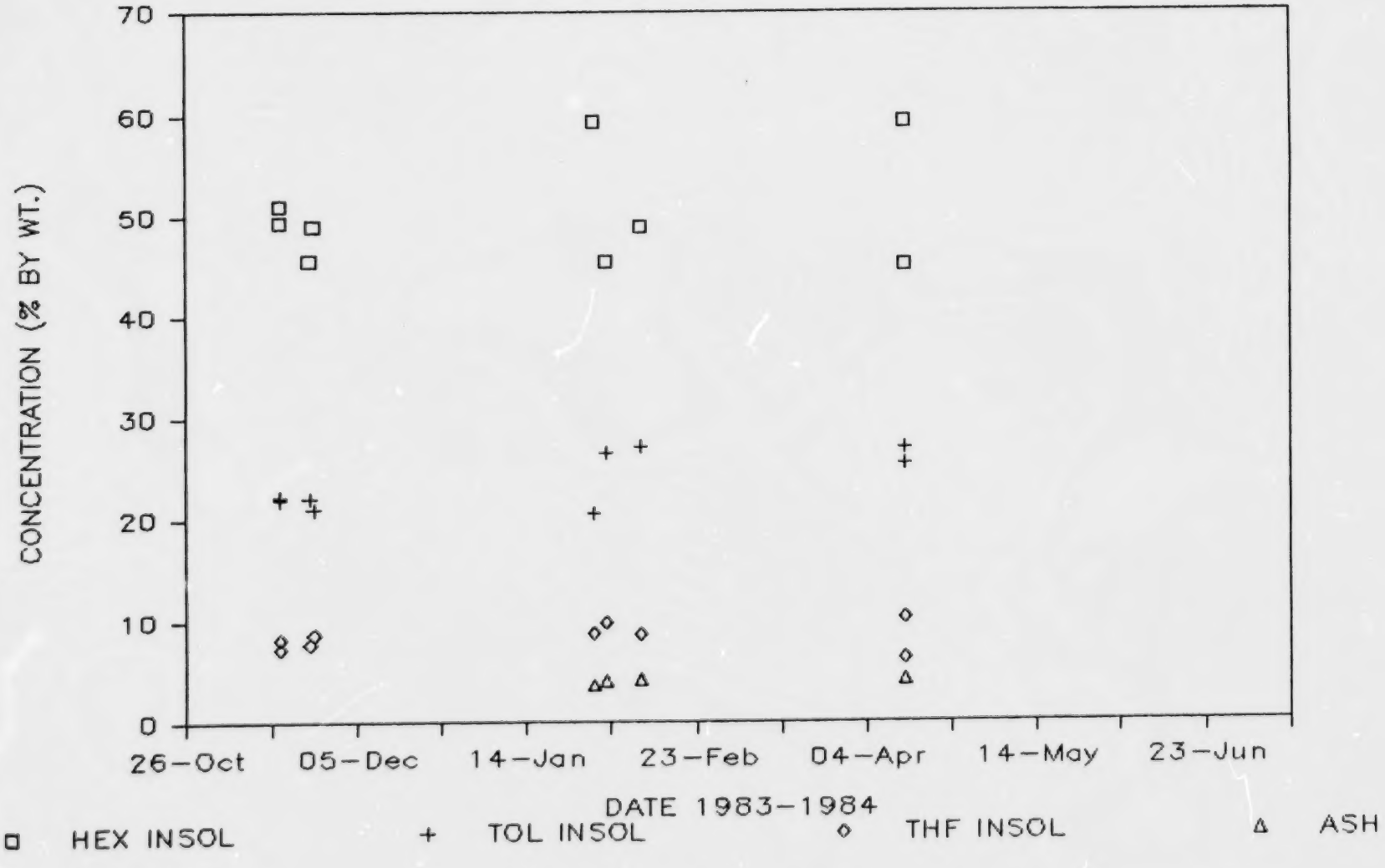


TABLE 4.2 V110 BTM 242 - REPEAT ANALYSIS

Insolubles	#of Analyses	Mean wt %	95% Confidence Range wt %	Standard Deviation
hexane	9	50.41	46.84 - 53.99	5.47
toluene	9	23.85	22.09 - 25.61	2.70
tetrahydrofuran	9	8.45	7.65 - 9.25	1.23
Ash	5	4.09	3.88 - 4.31	0.25

In addition, the results for V110 BTM 243 were compared to those obtained by the filtration method and the traditional soxhlet extraction method both employing the widely used solvents of cresol, benzene and pentane shown in colums 2 and 3 of Table 4.3.

The comparison of the data (columns 1 and 2) for filtration, indicates that use of the pentane, benzene and cresol results in slightly lower values for oils and unconverted coal and corresponding higher values for pre-asphaltenes and asphaltenes. This is due to the different properties of the solvents.

Comparison between filtration and soxhlet (columns 2 and 3) yield only marginally different results. This is probably due to the difference in the filtering performance of the soxhlet thimbles versus the filters.

The values of ash for columns 1, 2 and 3 are virtually equal. This illustrates the homogeneity of the samples and the degree of reproducibility of the ash determination.

The significance of the data presented in column 4 of Table 4.3 is discussed in detail in the following section.

TABLE 4.3 COMPOSITION OF FEED SAMPLE AS DETERMINED BY DIFFERENT ANALYTICAL METHODS*

Analytical Method	hexane toluene THF filtration	pentane benzene cresol filtration	pentane benzene cresol soxhlet	pentane** benzene cresol soxhlet
Composition (wt %)				
O	46.20	42.30	43.40	61.1
A	29.77	33.30	31.64	26.5
PA	14.38	17.30	15.45	4.3
UC	5.12	2.64	4.95	3.2
Ash	4.53	4.54	4.56	4.8

* Feed Material - V110 BTM 243
** Wilsonville Analysis (14)

4.2 Aging Due to Transportation and Storage

Normally, when working with fresh coal-derived products, the concentration of uncoverted coal as determined by boiling cresol and THF are comparable. The materials used in this report appear to have aged. This is confirmed by performing an analysis of V110 BTM 243 using boiling cresol as a solvent instead of THF. The results are summarized in Table 4.3.

Comparison of unconverted coal(UC) values in columns 1 and 2 indicates a significant increase of organic insolubles. These insolubles are called "quasi" solids and are defined here as compounds that are insoluble in THF and soluble in cresol. They are probably due to aging of the material where certain compounds re-combine to form higher molecular weight hydrocarbons.

Also shown in Table 4.3 (column 4) is the composition of V110 BTM 243 as reported in reference (14). Comparing the values to those in column 1, shows that there is a shift towards THF soluble material with a considerble decrease in oil and a marked increase in pre-asphaltenes. Oil decreased by 24% and pre-asphaltenes increased by 234%. This indicates that the material was unstable as there is a definite shift towards the higher molecular weight compounds from the lighter compounds i.e., hexane soluble towards THF insoluble.

The majority of the retrogressive reactions occurred prior to receipt of the samples and were due to transportation and storage. These have been minimized after receipt by the handling procedure developed which included limiting exposure to relatively high operating temperatures and oxygen and by storage at low temperatures.

4.3 Stability of Materials During Processing

The stability of feed materials during processing is an important consideration. Instability will not only comfound separation performance results but has a negative impact on the economics of the liquefaction process. As discussed in Section 4.2, the materials used in this research are unstable and since certain separation processes are known to cause a retrogression toward the higher molecular weight compounds, it is important to investigate the effect of the Centrax process on the materials used in this study. The areas where the investigation is centered on are:

- the pre-heating step where the material is heated and mixed,
- the separation/extraction step where the material is separated, and
- the extractant recovery step where the distillables are evaporated and subjected to high temperatures for short periods of time.

4.3.1 Stability

To investigate the stability during the pre-heating stage the following work was conducted. Starting materials were placed in a sealed centrifuge tube and heated to a specified temperature for a period of 1 hour. The temperatures employed were 200 and 300°C. A sample of V110 BTM 243 processed alone and with 30% T105 BTM were used for this investigation.

The conditions chosen were far more severe in temperature and residence time than would be actually encountered during the preparation stage. Processing V110 BTM 243 without extractant was chosen since it would be an extreme case with regard to extractant level. Using 30% extractant is a moderate case and was picked to investigate the stabilizing effect of the extractant.

The results are summarized in Table 4.4. The inital and final composition of the samples after holding at an elevated temperature for 1 hour were determined and normalized to 100 units on an extractant-free basis. The table presents the change of composition of the sample as a result of preheating.

TABLE 4.4 EFFECT OF TEMPERATURE AND EXTRACTANT ON FEED STABILITY

Feed Components	Change in Composition After 1 hour (200°C)		Change in Composition After 1 hour (300°C)	
	without extractant	with extractant	without extractant	with extractant
O	+0.9	-2.1	-4.1	+5.6
A	-1.1	+0.7	+3.9	-4.8
PA	+1.2	+2.2	+2.8	+2.2
UC (Quasi-Solids)	-1.0	-0.6	-2.4	-2.7
ASH	0.0	-0.2	-0.2	-0.9
Net Change	0.0	0.0	0.0	0.0

% change in composition based on normalized extractant-free basis
Feed - V110 BTM 243
Extractant - T105 BTM 243
Feed/Extractant Ratio 1:0.3

At 200°C there appears to be little change in the composition with or without the presence of extractant, certainly within the relative analytical error. However, at 300°C, changes in composition appear to be more significant. Without extractant, the effect of the 300°C temperature appears to have caused a decrease in oils, at the expense of an increase to higher molecular weight components. However, addition of the extractant seems to reverse this trend by increasing the oil concentration and decreasing the concentration of asphaltenes.

This experiment indicates that the presence of the process-derived extractant will result in the prevention of any retrogressive changes in feed composition and at higher temperature, may even have a beneficial effect.

4.3.2 Stability of Separation/Extraction Stage

Although no direct investigation of stability during this stage was performed, it is believed that the results and conclusions from the preparation stage are applicable.

This is because this operation is conducted at an identical temperature as the preparation stage and for a substantially shorter period of time. The sum of the residence times for both the separation/extraction and preparation stages would be less than the 1 hour used for the investigation as outlined in Section 4.3.1.

Therefore, since the material was stable during that investigation, it is expected to be stable during the separation/extraction stage.

4.3.3 Stability of Products during Extractant Recovery Stage

In order to investigate the stability of materials during the extractant recovery stage an experiment was conducted processing four different feeds. These feeds were the distillate fraction of V110 BTM (100% Oil), the first and second separated liquid phases from a separation/extraction stage (asphaltene & pre-asphaltene rich), and a compacted solids phase after two successive separation/extractions (solids and oil primarily). These materials were selected to allow for an evaluation of the changes of the different components in this process step.

The results of this experiment are summarized in Table 4.5 Changes in feed as a result of processing through the recovery unit have been calculated. The product streams from the unit are a liquid stream consisting primarily of oil and a solids phase ash concentrate that is 100% THF insoluble. The composition of these streams are compared to the feed.

The relative change in the oil fraction is small. This indicates that the oil fraction is generally stable and does not degrade during the extractant recovery stage.

In the case of the asphaltene and pre-asphaltene components it appears that these constituents degrade during the extractant recovery stage and form THF insoluble material. This is readily seen by comparing the change in unconverted coal values for the feed having pre-asphaltene and pre-asphaltene components. In each case the unconverted coal value increases whereas the asphaltene and pre-asphaltene values decrease. Some production of gaseous compounds is believed to have occurred and is determined by the material losses.

It is important to note that some asphaltenes and pre-asphaltenes are recovered during this step.

TABLE 4.5 STABILITY OF COMPONENTS IN THE EXTRACTANT RECOVERY STAGE USING FEEDS OF VARYING COMPOSITIONS

			Change in Composition					
	V110 BTM 243 (IBP - 500°C)		Separated Liquid Phase		Separated Liquid Phase		Compacted Solids Phase	
Components (wt %)	Feed	Change	Feed	Change	Feed	Change	Feed	Change
O	100.00	-1.03	75.91	- 6.36	54.67	+6.53	42.18	+3.28
A	0	+ 0.13	15.04	-12.13	27.62	-13.34	4.98	-9.91
PA	0	+ 0.90	7.59	- 5.43	15.39	-13.56	6.72	
UC	0	0.00	1.42	+ 22.41	2.07	+ 18.58	19.68	+3.76
Ash	0	0.00	0.04	+ 1.14	0.26	+ 0.36	26.44	-1.48
Losses (Gases)		0.00		+ 0.37		+ 1.42		+4.35

In a typical Centrax process configuration, the only stream which is processed in the extractant recovery stage is the compacted solids phase. Although gas production is relatively high for this example, it is expected that with process optimization, this can be reduced to essentially zero. Similarly, it is expected that the production of unconverted coal (coke in this case) can be minimized further.

5.0 ANALYTICAL AND EXPERIMENTAL PROCEDURE

As discussed in Section 3, the analytical and experimental procedures underwent extensive development throughout the research program. The following sections are descriptions of the final developed analytical and experimental procedures.

5.1 Analytical Procedure

5.1.1 Handling of Samples

The samples received were handled in the following manner:

1) Samples were weighed and visually inspected and recorded.

2) Each sample was sub-sampled in order to provide a practical working sample (as outlined in Section 5.1.2). In addition, a one litre sample of each was retained as a reference.

3) Working samples were stored in a freezer whereas the bulk samples were stored at room temperature in a storage room.

5.1.2 Sampling

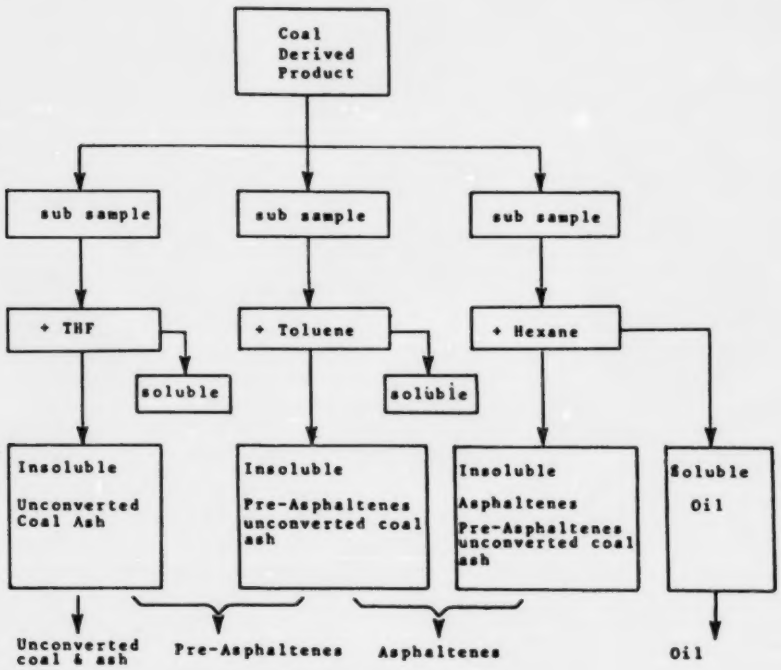
Since most of the products encountered are heterogeneous in nature, specific sampling techniques must be employed. The actual method used was dependent on the physical nature of the sample at room temperature. Relatively fluid samples were stirred mechanically prior to sampling to ensure homogeneity. Highly viscous materials were warmed for ease of mixing then mixed and sampled. Solids were either crushed and sampled, or melted, flaked and sampled depending upon the nature of the sample analyzed (caution was exercised to ensure that the excessive heating did not occur which would alter sample compositions).

5.1.3 Analysis

Coal-derived products are considered to consist of solids, preasphaltenes, asphaltenes and oils. These are generally characterized by their solubility in different solvents(2-8). The use of a solubility classification method is dependent on certain key factors. The main factors are: versatility of use on different materials, extraction of all soluble material, precision and speed of characterization. In this report solids are considered to be that fraction which is insoluble in tetrahydrofuran (THF) and consists of unconverted coal and ash. Preasphaltenes are those that are soluble in THF but insoluble in toluene whereas asphaltenes are soluble in toluene but insoluble in hexane. The hexane-soluble portion is considered to be oil.

As illustrated in Figure 5.1, the classification of a coal-derived product was classified by determining its solubility in each solvent and then calculating each fraction by difference. Solvent extractions and insoluble collection was performed by vacuum filtration which allows for immediate analysis using solvents of relatively low toxicity and without the need for using the time consuming soxhlet extraction technique. Separate samples were used for each analysis.

FIG. 5.1 ANALYSIS SCHEMATIC



For each analysis a sample was weighed into a beaker and dissolved by an excess (40 to 50 times the sampled weight) of the appropriate solvent. Maximum solvent extraction was accomplished by stirring the sample vigorously on a hot plate near the boiling point of the solvent for a minimum of thirty minutes.

The samples were allowed to cool to room temperature and then were filtered under vacuum using a pre-weighed filter. The filters employed were Whatman 934H (glass fibre circles), Whatman 42 (cellulose) and Millpore membrane type (polyvinylidene difuoride). The filter cake was washed with an excess amount of solvent and then dried in an oven until constant weight is achieved.

Ash was determined by igniting the THF, toluene and/or hexane insolubles at 925°C for a period of 1 hr as per ASTM 1553-73 1982. Since the filters were ashless, both the filter and filter cake were ignited.

Simulated distillation has been used here as a method for obtaining boiling point data of the liquid fraction of the hydrocarbon slurries, in addition to vacuum distillation data.

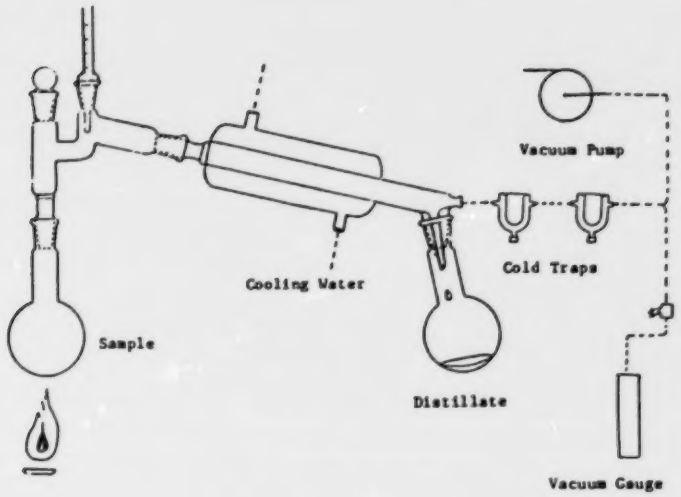
The simulated distillation system used consisted of a Perkin-Elmer Sigma 3 chromatograph with dual FID detectors and a Sigma 10 data acquisition console. The columns used were 61 cm long, 0.32 cm diameter, stainless steel, packed with 10% SP2100 on 60/80 supelco-port.

column temperature	- initial	: 60°C
	- final	: 340°C
	- rate	: 8°C/min
detector temperature		: 350°C
injector temperature		: 350°C
carrier gas		: N_2
sample size		: 0.2 - 1.0 µl
analysis time		: 35 min

Calibration was accomplished with a mixture of n-paraffins from C_7 to C_{40} covering the boiling range 60°C to 525°C.

Vacuum distillations were conducted using a system based on the one illustrated in ASTM D 1160-77. The actual system is shown in Figure 5.2.

FIG. 5.2 VACUUM DISTILLATION APPARATUS



5.2 Experimental Procedure

5.2.1 Preparation of Feed and Extractant

Generally the feed consisted of a homogeneous portion of the sample to be investigated. This was accomplished as outlined in Section 5.1.2. Extractants that were used for these experiments consisted of the distillable fractions of the feed material and T105 BTM 243. Distillations were performed by vacuum evaporation as per Section 5.1.3.

5.2.2 Lab-Scale Separation/Extraction Experimental Procedure

The separation process is defined as consisting of three stages (as shown schematically in Figure 5.3). These are pre-heating, separation and extractant recovery. During the pre-heating step, the starting material (feed and extractant) is heated and mixed. In the separation step the mixture is divided into two streams, a separated liquid phase, rich in preasphaltenes and asphaltenes and a compacted solids phase, concentrated in solids.

Additional separations/extractions can be carried out on the compacted solids phase and/or separated liquid if required.

5.2.3 Pre-Heating

The feed was placed into a centrifuge shield. If required, a predetermined amount of extractant was added and the tube is placed in a oil bath. The oil bath was heated from room temperature to the desired temperature and when the mixture melted, the paddle end of a spatula was used to blend and agitate the mixture. It is mixed continuously until the required temperature is reached. For example, a temperature of 180°C required 20 minutes heating time from room temperature.

At this point, the mixer was removed and carefully scraped making sure that the removed material falls down into the mixture. This was done not only to limit material losses but to maintain the original sample composition since certain constituents preferentially adhered to the mixer. They were probably preasphaltenes and asphaltenes.

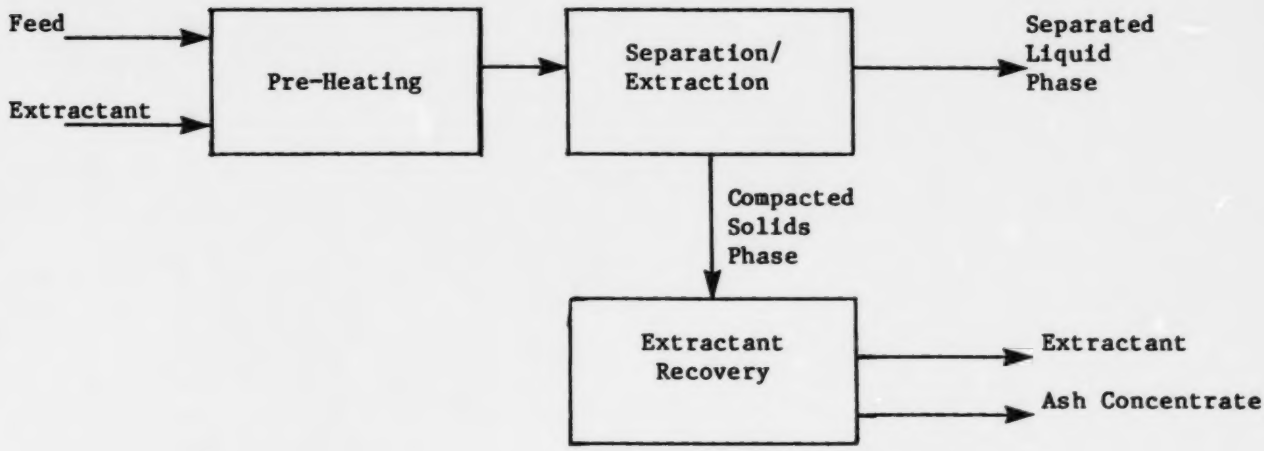
5.2.4 Separation/Extraction

The separation/extraction step was carried out in a modified laboratory centrifuge. It was brought up to temperature during the pre-heating step of the shield and its contents. When both the centrifuge and the shield were at the prescribed temperature, the shield was transferred from the oil bath and placed in the trunion ring of the head. Also transferred to the centrifuge was a preheated counter balance. During the transfer, care was taken that neither the mixture nor the centrifuge cooled down. The centrifuge temperature was achieved and maintained by blowing hot air into the bowl. The shield was processed at a selected speed and for a predetermined length of time.

Immediately on completion, the top layer was decanted into a receiver before the mixture cools. Care was taken not to remix the two layers during this procedure. The bottom layer remained in the tube and was allowed to cool to room temperature.

This step constituted a single stage separation but if additional separations/extractions were necessary, the compacted solids phase or seqarated liquid phase could be processed one or more times through the procedure outlined previously.

FIG. 5.3 SCHEMATIC OF SEPARATION/EXTRACTION PROCEDURE



5.2.5 Extractant Recovery

Extractant recovery was accomplished by flash evaporation of distillables from the compacted solids phase. Flash evaporation was carried out at atmospheric pressure. As described earlier, evaporated vapours are removed from the high temperature environment almost instantaneously by an inert gas.

The flash evaporation unit is shown schematically in Figure 5.4. It consists of an inclined stainless steel plate enclosed by a housing complete with nitrogen purge, inlet and outlet ports. The plate temperature and evaporator inside temperature are monitored by thermocouples. Condensers and gas traps are connected in series to the exit port. A piston-type injector is used to introduce the compacted solids phase into the unit.

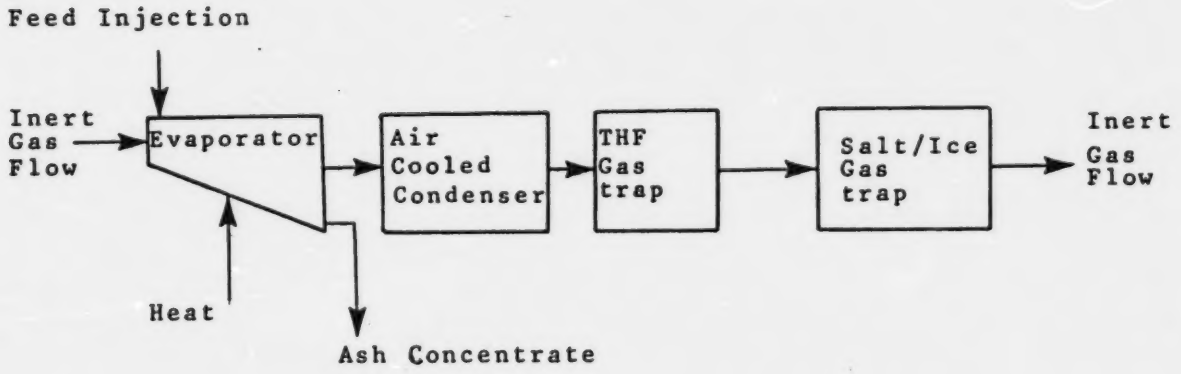
The plate is inclined to the desired angle and heated. The angle is such that it allows the feed to flow in a thin layer down the entire length of the plate, where the oils are evaporated and swept away by the nitrogen purge. Too shallow an angle will result in the feed staying "en masse" below the injection port. Conversely, too steep an angle will result in the compacted solids phase rolling or running down to the bottom of the plate where it collects. This results in the formation of a thick layer at the bottom which still contains a significant liquid fraction. The plate temperature in this region is probably too low to recover these liquids and there is evidence that distillable material tends to become entrapped in the bulk of the

residue where it undergoes thermal degradation. A low temperature will result in a higher residence time thereby increasing the probability of degradation. A higher than required temperature will probably promote thermal cracking. All these conditions are undesirable.

In the studies conducted with the flash evaporation unit, a nitrogen purge carried the distillables through the condensers and into the THF filled gas trap. Most of the oils were collected in the condenser with the remainder dissolving into the THF as the gas passes through.

The oil was recovered by washing the condensers and gas trap with THF. The residue left on the plate is ash concentrate and was manually scraped off. It is a dull grey, friable and porous solid. A small amount of non-injected material was removed from the injection system by THF washing.

FIG. 5.4 LABORATORY EXTRACTANT RECOVERY SYSTEM



6.0 RESULTS AND DISCUSSION; SINGLE STAGE OPERATION

6.1 Coal Product Description and Characterization

A variety of coal products from the Wilsonville Coal Liquefaction plant were used in this investigation. Found in Appendix 2 are process flow diagrams of the Wilsonville facility as it applies to products studied here.

6.1.1 V110 BTMS 242 and V110 BTMS 243

The materials designated as V110 BTMS 242 and V110 BTMS 243 were samples of the bottoms from flash tank V110 from the Wilsonville Pilot Plant experimental runs 242 and 243 respectively. The choice of these process streams as feed material for the Centrax evaluation are described in Section 2.3.

The materials were shiny black solids at room temperature. The physical state and composition of these products dictated that special handling procedures had to be used. To achieve homogeniety, each had to be melted and mixed before using. Since some coal products are characteristically unstable where compounds tend to revert to higher molecular weight units as outlined in Section 4, heating and reheating is believed to accelerate this trend. To limit the number of heatings that are dictated by the numerous experiments scheduled, the following procedure was used. Both materials were melted ($\sim 110^{o}C$) and each lot was stirred and mixed with a mechanical mixer until a homogeneous slurry was formed. Each mixture was then flaked. In the final step, the flakes were frozen, ground in a mill and subsequently mixed. In the ground state these coal products were found to be extremely workable in addition to being more representative than in their original form.

Each product was analyzed to determine the content of oil, asphaltenes, preasphaltenes, unconverted coal, and ash. Analyses were performed as outlined in Section 5.1.3 and are summarized in Table 6.1.

Vacuum distillations were performed to produce distillate fractions. These distillate fractions were analyzed by the simulated distillation technique. Results are summarized in Figure 6.1 in the form of bar charts showing percentages of different boiling fractions normalized to 100% of the vacuum distillable fraction.

The results reveal that V110 bottoms from runs 242 and 243 are quite similar materials. As shown in Table 6.1, the oil content is very similar 49.6% and 46.2% for runs 242 and 243 respectively. From Figure 6.1 it is seen that there is some difference in the boiling point distribution of the distillates of the V110 bottoms between runs 242 and 243 . Overall, run 242 appears to be lighter (62.8% less than $400^{o}C$ compared to 44.6%).

6.1.2 T102 BTMS 242 and T102 BTMS 243

Designated as T102 BTMS 242 and T102 BTMS 243 were samples of the bottoms from vacuum tower T102 where the distillation of V110 BTM 242 and V110 BTM 243 material was conducted for experimental runs 242 and 243 respectively.

The bottoms of T102 is the feed to the Critical Solvent Deashing Unit. These materials were reddish-brown in colour and already crushed into a workable form. Sampling was accomplished by coning and quartering which is an established practice of mixing and splitting to reduce the bulk of a solids sample.

Analyses were performed as per Section 5.1.3 and the results are listed in Table 6.1.

6.1.3 T105 BTM 243

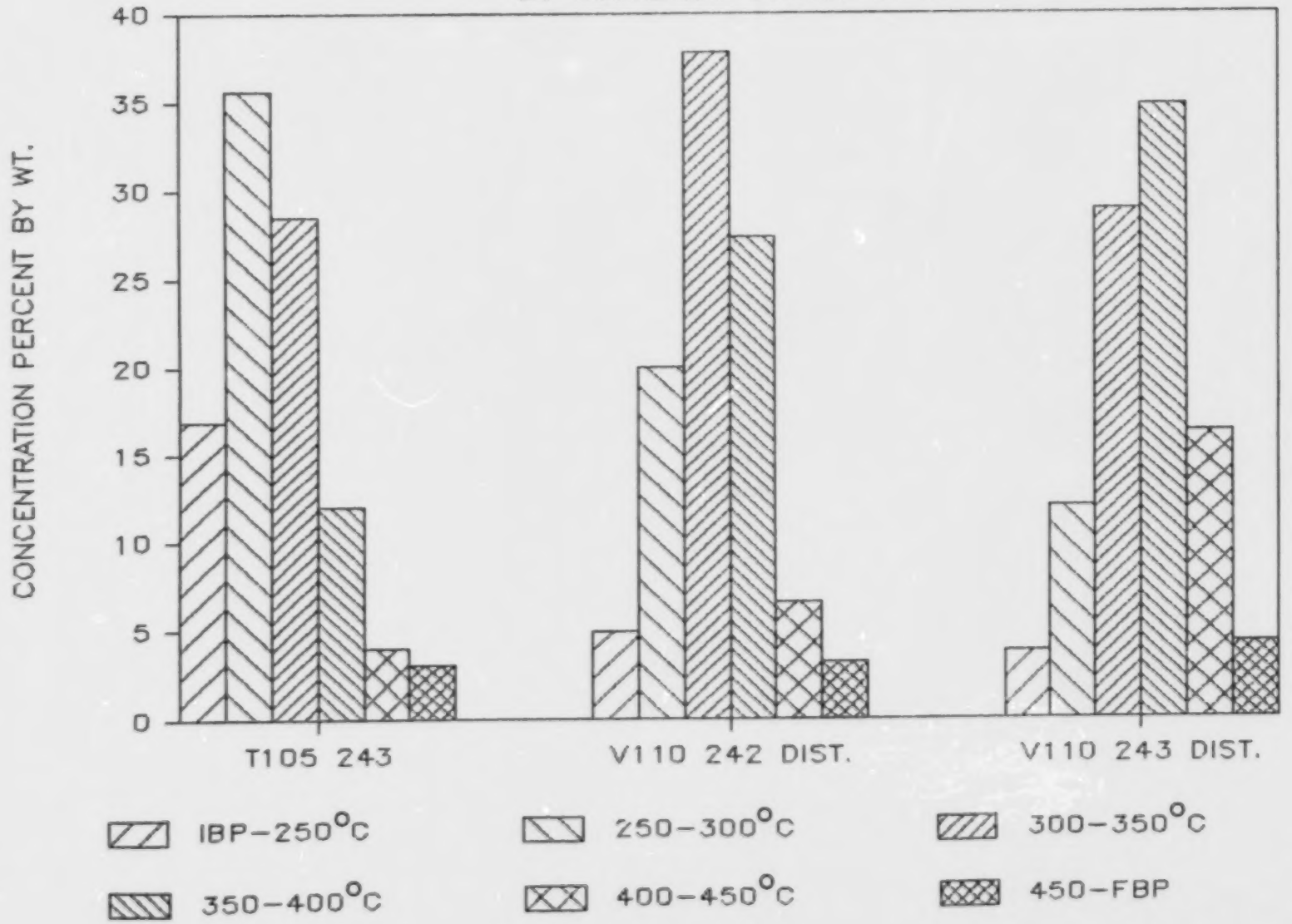
Product T105 BTMS 243 is the bottoms from distillation tower T105 located in the hydrotreating unit and is designated as "hydrotreated solvent". At room temperature its physical appearance it is a clear amber liquid. On analysis it was found to be 100% hexanes soluble (100% oil). A simulated distillation resulted in an Initial Boiling Point (IBP) of 180°C and a final boiling point of 508.8°C. Found in Figure 6.1 is the resultant distillation curve presented in the form of a bar chart. T105 bottoms are used as a recycle solvent in the SRC unit. Thus, a large proportion of the V110 BTM contains T105 BTM material. A sample of T105 BTM for experimental run 242 could not be obtained as it was unavailable at the time of request.

TABLE 6.1 ANALYSIS RESULTS OF WILSONVILLE LIQUID COAL PRODUCTS AS RECEIVED

Process Stream	Components (wt %)				
	O	A	PA	UC	Ash
V110 BTM 243	46.20	29.77	14.38	5.12	4.53
V110 BTM 242	49.59	26.56	15.40	4.36	4.09
T102 BTM 243	12.70	48.94	25.22	7.60	5.54
T102 BTM 242	14.36	42.39	31.69	5.80	5.78
T105 BTM 243	100.00	-	-	-	-

FIG. 6.1 BOILING POINT RANGE

BY SIMULATED DISTILLATION



6.2 Process Variables - Single Stage Separation/Extractions

A large number of experiments were conducted to both develop the analytical and experimental procedures and to investigate the effect of process variables during the separation/extraction stage and liquid recovery stage. The materials used for this study were V110 BTM 243, V110 BTM 242, T102 BTM 242, T102 BTM 243 and various process-derived extractants.

For the separation/extraction operation, the dependent variables (Centrax performance criteria) studied were:

- ash concentration of separated liquid
- precipitation of asphaltenes and pre-asphaltenes
- compressibility of separated solids

and the investigated independent variables were:

- type of extractant
- amount of extractant
- process temperature
- centrifugal force
- residence times

The effect of each independent variable on the performance criteria are discussed below.

6.2.1 Ash Concentration of Separated Liquid

The ash content of the separated liquid is measured by the ash concentration of the overflow. Minimum ash content is desirable for better operability in possible downstream upgrading of this product.

Type and Amount of Process-Derived Extractant

Illustrated in Figure 6.2 are the resultant ash concentrations from a series of experiments (43,45 and 46) investigating the effect of type and amount of extractant combined with the same feed on ash separation efficiency.

The feed material was V110 BTM 243 and the extractants investigated were:

T105 BTM 243

V110 BTM 243 - IBP to 400^{o}C fraction

V110 BTM 243 - IBP to 500^{o}C fraction

Four feed to extractant ratios were used:

A	1 : 0.2
B	1 : 0.5
C	1 : 1
D	1 : 3

The feed/extractant mixture was centrifuged at 1800 Gs at 180°C for 5 minutes.

The use of T105 BTM 243 results in zero ash content in the separated liquid phase for all concentrations investigated. The distillate of V110 BTM 243 IBP-500°C used as extractant results in a minimum of zero ash concentrations at extractant levels of 0.5 and 1. Higher ash levels of 0.04% and 0.01% are produced with mixtures of 1:0.2 and 1:3. The use of V110 distilate IBP-400°C results in significantly higher ash values of 0.05% to 0.11%. The minimum ash level occurred at a feed:extractant ratio of approximately 1:0.5.

For V110 BTM 243 material:

- Ash levels of zero can be achieved in the liquid overflow at feed:extractant levels of 1:0.2 to 1:3 using T105 BTM 243 as extractant compared to ash values of 0.5 - 1.0% when no extractant was used.
- Utilization of V110 distillate IBP-500°C achieves zero ash levels at extractant levels of 1:0.5 and 1:1.
- A zero ash level was not achieved with the use of V110 distillate IBP-400°C but a minimum of 0.05% was obtained at a ratio of 1:0.5.

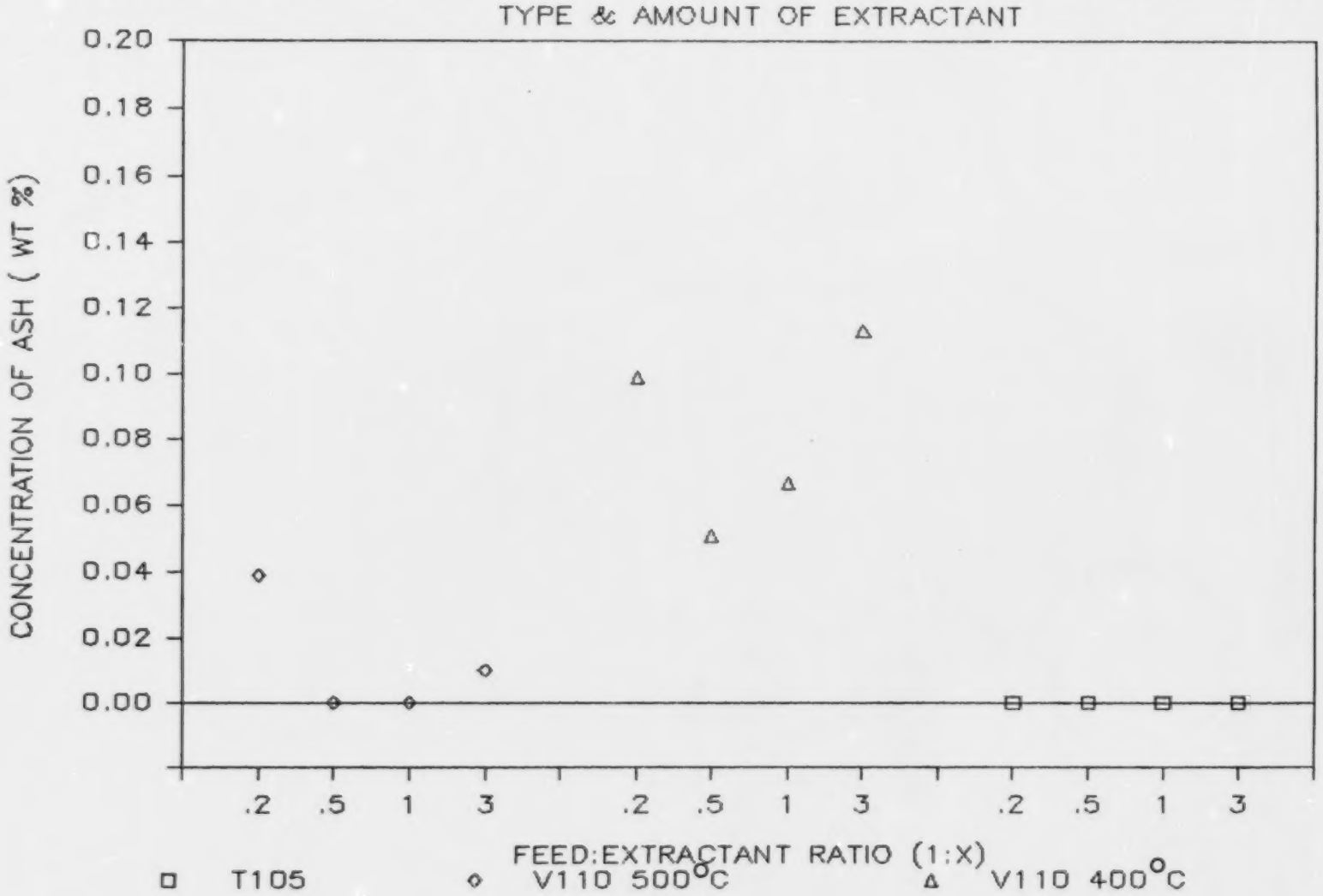
Non-Process-Derived Extractants

The effect of non-process extractants is illustrated by Table 6.1 where V110 BTM 243 is processed with xylene, toluene and a light fraction (250-300°C) of T105 BTM 243.

TABLE 6.2 ASH CONCENTRATION OF SEPARATED LIQUID

	V110 BTM 243 to Extractant Ratio 1 : 1	1: 0.1
Type of Extractant		
Toluene	0.00%	1.40%
Xylene	NA	1.25%
T105 BTM 243 (250-300°C)	0.38%	1.21%

FIG. 6.2 ASH CONTENT—SEPARATED LIQUID



At an extractant to feed ratio of 1 : 1 for toluene, the ash concentration in the overflow was 0.0 and 0.4% for a light cut of the T105 BTM material. However, by reducing the amount of extractant used, the quality of the separated liquid deteriorated such that the ash concentration was between 1.2 and 1.4% for the toluene, xylene and the light process-derived cut.

These tests were performed at lower temperatures than the experiments with process-derived extractants. The volatile nature of these pure components required lower temperatures.

The high ash levels for the separations with toluene, xylene and T105 BTM 243 (250-300°C) may be a consequence of the different interaction between these types of extractants and the mixture of solids, pre-asphaltenes, asphaltenes and oils. At higher feed:extractant ratios, the addition of these dissimilar materials, enhances precipitation of the asphaltene/pre-asphaltene components thereby promoting the ash removal at the cost of both the loss of separated liquid products and processing relatively large amounts of extractant. The precipitation of pre-asphaltenes through the use of non-process-derived extractants is discussed in Section 6.2.2.

- The use of non-process-derived extractants at economical ratios of feed to extractant, results in poor ash separation.

Type of Feed

Figure 6.3 compares the ash concentrations of the separated liquid resulting from the processing of various feeds. These feeds include, V110 BTM 242, V110 BTM 243, T102 BTM 242 and T102 BTM 243. T102 BTM type material was not studied extensively since it was deemed to be an unlikely candidate as a feed to the Centrax Process. Extractant used for the type of feed investigation was T105 BTM 243.

For processing T102 bottoms, which is the same material as V110 bottoms material, except that a large portion of distillates have been removed in the vacuum tower at Wilsonville, the ash concentration was very high for the case of centrifuging without extractant. Ash levels of 5% were recorded for this material for both runs 242 and 243. In comparison, the retention of the distillate in the V110 BTM gives much lower ash concentrations, on the order of 1% for run 243 and 0.1% for run 242 material. The difference between runs 242 and 243 may be accounted for by the different processing arrangements which affect the nature of the solids and physical characteristics of the liquid fraction.

For the T102 BTM material, 50% extractant was required to produce an ash-free separated liquid. However, with V110 BTM material, an ash-free separated liquid was achieved with extractant additions between 10% and 30%.

FIG. 6.3 ASH CONTENT—SEPARATED LIQUID

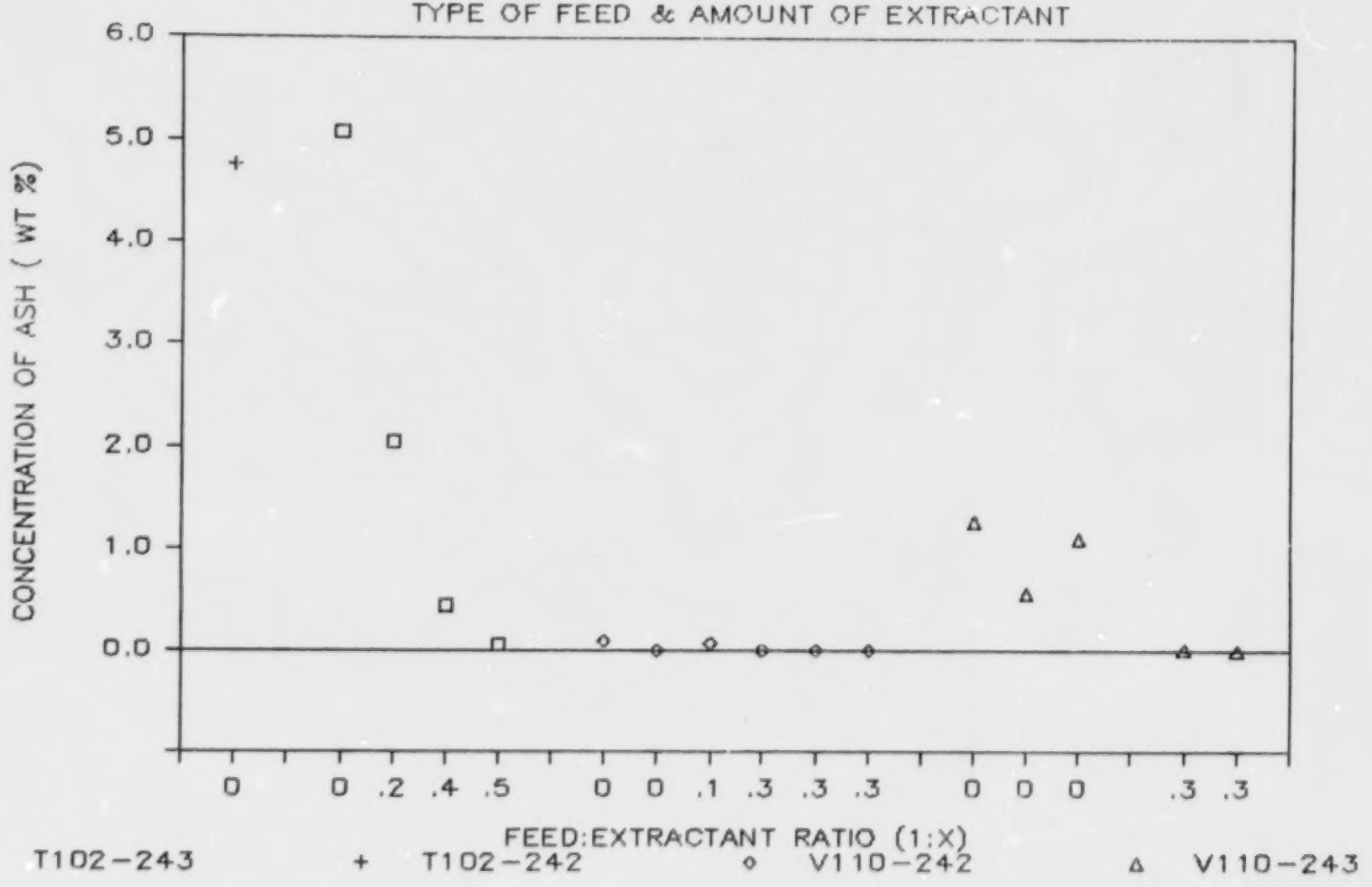
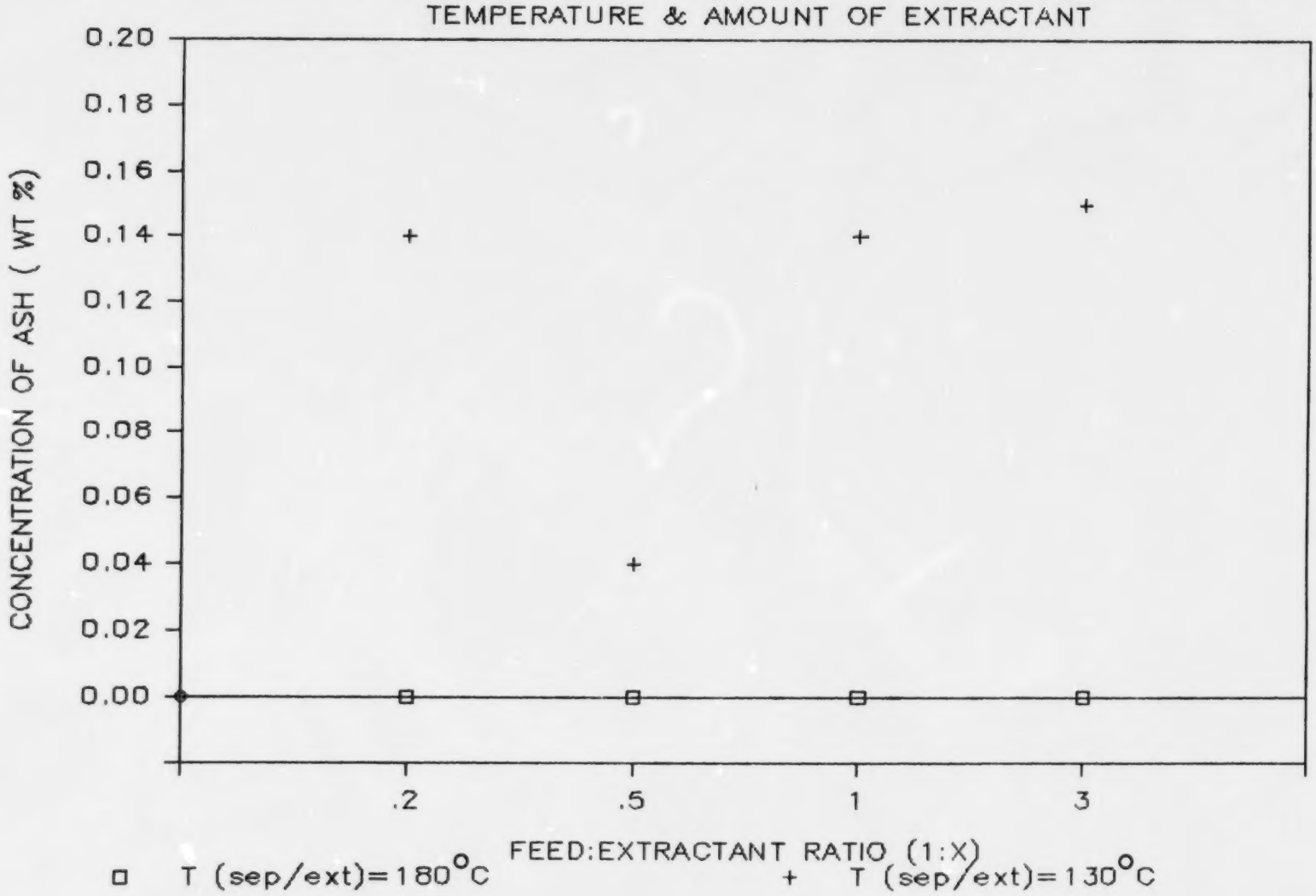


FIG. 6.4 ASH CONTENT—SEPARATED LIQUID



In conclusion:

- Different feeds exhibit varying separation characteristics which can be minimized through control of process parameters.

Temperature

Figure 6.4 shows the effect of processing V110 BTM 243 at 130°C compared to 180°C for a range of extractant levels.

The results indicate:

- At 180°C, zero ash in the overflow was achieved, but at 130°C, the minimum ash in the overflow was only 0.04% with the majority of results in the 0.15% range.

- A significant increase in ash concentration resulted when the material was processed at 130°C.

Temperature is expected to have an effect on the separation of ash particles since hindered settling velocity for a particle is proportional to Stokes' Law.

$$U_t \propto \frac{\omega^2 r (\rho_p - \rho) D_p^2}{18 \mu} \qquad (1)$$

Ut	-	terminal hindered settling velocity
ω	-	rate of rotation
ρ_p	-	density of solid
ρ	-	density of liquid
Dp	-	equivalent diameter of a spherical solid particle
μ	-	liquid viscosity
r	-	radius of rotation

Both u and p are temperature dependent with viscosity particularly dependent on temperature (T), i.e., $u = f(e^{-\frac{1}{T}})$.

At higher temperatures the terminal settling velocities are considerably higher which enhances the removal of smaller particles.

Centrifugal Force and Separation Residence Time

The investigation of centrifugal force was conducted by processing V110 BTM 243 and T105 BTM 243 in a ratio of 1:0.1 using separation forces of 1800 and 700 multiples of gravity. This force was achieved

by operating the centrifuge as described in Section 3.2 at speeds of 3200 and 2000 RPM. Two residence times of 5 min and 10 s were used. The results of this investigation are represented in Table 6.3.

TABLE 6.3 ASH CONCENTRATION OF SEPARATED LIQUID

	Separation Residence Time	
	5 min	10 s
Centrifugal Force		
1800 G	0.18 %	1.78%
700 G	1.24%	2.37%

As can be seen in Table 6.3, the most complete separation as illustrated by an ash concentration in the separated liquid of 0.2% resulted at process conditions of 5 minutes residence time and maximum centrifugal force. The poorest results of 2.4% were those achieved at the shortest residence time and a G force of 40% of the maximum.

Compared to best result conditions,

- A sixfold increase in ash content was witnessed when G force was reduced by a factor of 2 1/2.
- A ninefold increase in ash content was apparent when residence time was reduced by a factor of 30.
- A twelvefold increase when both the G Force and time were reduced.

The relationship between ash separation and centrifugal force is as expected. This is seen by inspection of equation (1) which illustrates the relationship between settling velocity and centrifugal speed. It is apparent that particles will have substantially reduced velocities at lower rotational speeds. In the case of settling velocities of the smaller particles, they may have insufficient time to travel from the top of the liquid layer down into the solids phase which is compounded by both reduced residence time and reduced centrifugal force. This same argument is directly applicable to the case of reduced residence time i.e., insufficient time for the smaller particles to travel the length of the liquid layer at the terminal velocities set by the processing conditions.

Pre-Heating Residence Time and Separation Residence Time

Shown in Table 6.4 are results from an investigation of the effect of residence time during the preparation step. Residence times of 20 minutes and 30 seconds were used . Mixtures of V110 BTM 243 and T105 BTM 243 in a ratio of 1:0.2 were processed at separation residence times of 5 minutes and 10 seconds at a temperature of 180°C and maximum separation force (1800 Gs).

TABLE 6.4 ASH CONCENTRATION OF SEPARATED LIQUID

	Separation Residence Time	
	5 min	10 s
Pre-Heating Residence Time		
20 min	0.12% , 0.02%	1.09%
30 s	0.14%	2.00%

To conduct the experiments at 30 seconds pre-heating residence time, a specialized procedure different from that outlined in Section 5.2 had to be enployed.

The procedure was to heat the feed material to 150°C, then add the extractant and finally plunge the mixture into a 180°C oil bath for the prescribed length of time. The mixture was stirred throughout this procedure. Separation was carried out as outlined in Section 5.2.

In the case of separation residence time of 5 minutes, no difference in ash concentrations of the separated liquid is noted. However, any effects caused by the difference in pre-heating procedure and residence time may be masked by the long separation residence time. At short separation residence time a difference of 1.09% and 2.00% is noted. Since the separation procedure was identical for these two experiments, it appears that this difference is a result of the pre-heating residence time.

This observation is preliminary and tentative, since it is based on very few data points. It does, however, indicate that there may be an effect on the ash separation efficiency but more data is required to come to a more definite conclusion.

6.2.2 Precipitation of Pre-Asphaltenes and Asphaltenes

The removal of ash from coal liquids is only part of the liquid/solid separation problem. The recovery of liquids from the separated solids is also very important. This is of particular significance in the case of deashing coal liquids, where the liquid product is very valuable and where over 60% liquid recovery is required just to separate the recycle solvent before any net coal liquefaction product is recovered.

The secret to high levels of product recovery is the separation of high molecular weight material, asphaltenes and pre-asphaltenes, from the solids, since mixtures having a large proportion of pre-asphaltenes and solids are nearly unseparable. Processes such as, vacuum distillation, anti-solvent deashing (ASD) and critical solvent deashing (CSD) achieve a high level of solids separation but poor liquid recovery due to the co-precipitation of pre-asphaltenes with the solids. Thus, the objective of Centrax Deashing is the deliberate prevention of the concentration of pre-asphaltenes with the separated solids. Concentration of pre-asphaltenes can be caused by removal of oils by evaporation or the precipitation of pre-asphaltenes known to be caused by anti-solvent type hydrocarbons.

In evaluating the performance of a given extractant and the conditions of Centrax processing, the extent of pre-asphaltene precipitation is a valuable indicator of the total liquid product recoverey effectiveness.

The most convenient means of monitoring pre-asphaltene precipitation is by the liquid concentration of oil, asphaltenes and pre-asphaltenes in the separated liquid after processing with an extractant. This is done on a solids and extractant free basis.

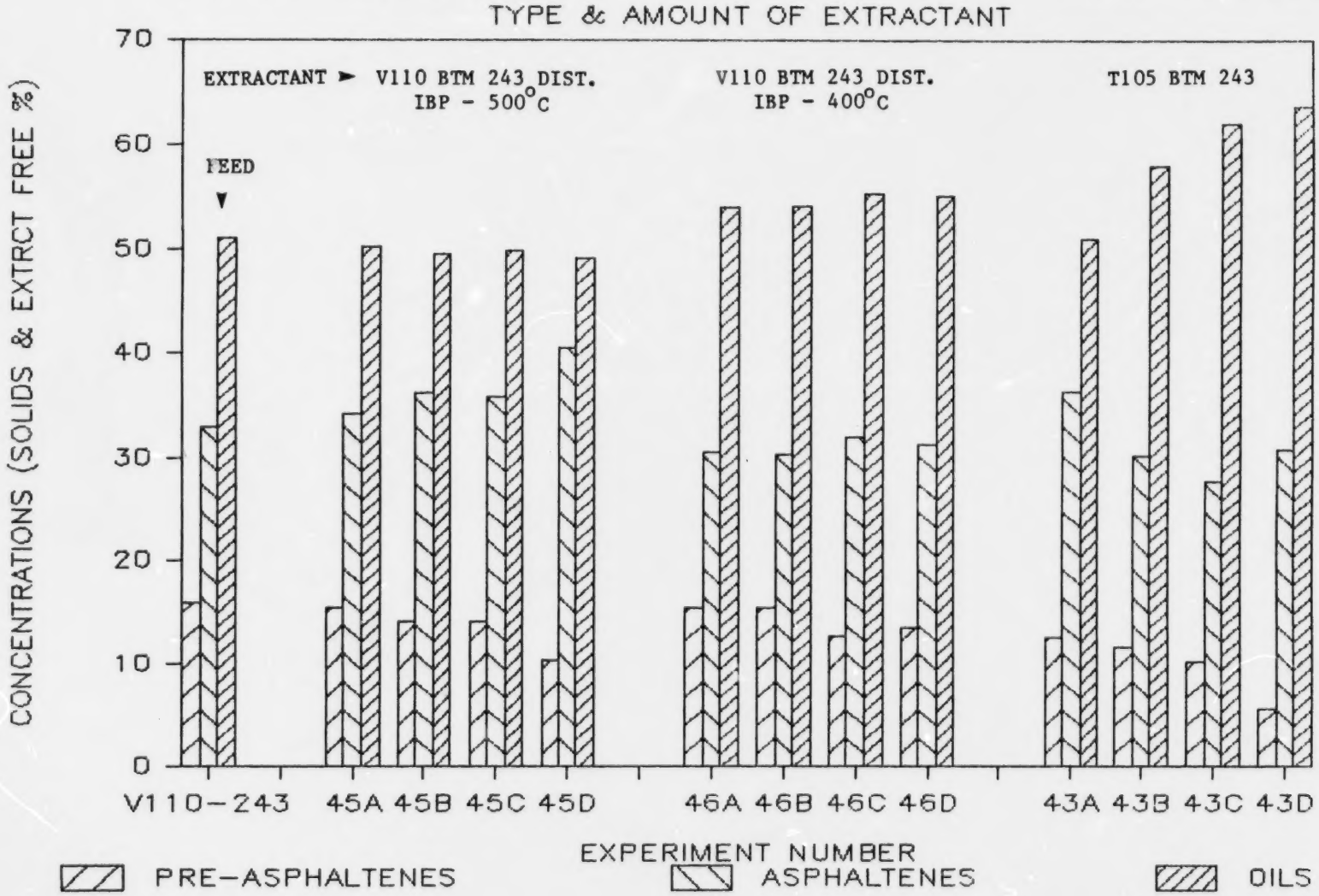
If no precipitation occurs, the relative concentrations of liquid components (O, A, PA) should be unchanged after processing. However, if the extractant or the processing conditions caused precipitation of pre-asphaltenes, the relative proportions of O, A and PA will be altered such that, the relative pre-asphaltene concentrations will be lower and the relative concentrations of oils and asphaltenes will increase in the separated liquid phase.

In this section, these relative concentrations of O, A, and PA have been plotted graphically to illustrate the effect of extractant and processing conditions.

Type and Amount of Extractant with V110 BTM 243 as Feed

A series of experiments were conducted using V110 BTM 242, V110 BTM 243, T102 BTM 242 and T102 BTM 243 using a variety of process-derived materials as extractants.

FIGURE 6.5 PRECIPITATION OF ASPHALTENES AND PRE—ASPHALTENES



Shown in Figure 6.5 are the results of experiments processing V110 BTM 243 as feed material with each of three extractants, namely: T105 BTM 243 (Exp. 43A, B, C, and D), V110 BTM 243 distillate IBP-500°C (Exp. 45A, B, C, D) and V110 BTM distillate IBP-400°C. Each of these extractants was mixed with the feed in the following ratios: 1:0.2, 1:0.5, 1:1 and 1:3.

The use of T105 BTM 243 as an extractant (Exp. 43A through 43D) results in the steepest trend of increased precipitation with increased amounts of extractant. The distillate of V110 BTM 243 IBP-500°C exhibits the smallest increase of precipitation of the three extractants studied (Exp. 45A through 45D). T105 appears to possess the poorest solvent properties which is accentuated when large amounts are used. It appears that the IBP-500°C fraction of the distillate of V110 BTM 243 displays good solvent properties over a wide range of mixture ratios. Distillate of V110 BTM 243 IBP-400°C exhibits solubility properties between those of T105 BTM 243 and distillate V110 BTM 243 IBP-500°C when mixed with V110 BTM 243 as feed (Exp. 46A through 46D).

In general, it is seen that precipitation occurs when relatively large amounts of T105 BTM 243 and V110 BTMs 243 distillate (IBP-400°C) are used. This does not occur when V110 BTM 243 distillate (IBP-500°C) is used as extractant.

Type and Amount of Extractant with Different Feeds

Different types of feed were investigated. These include V110 BTM 242, T102 BTM 242 and T102 BTM 243.

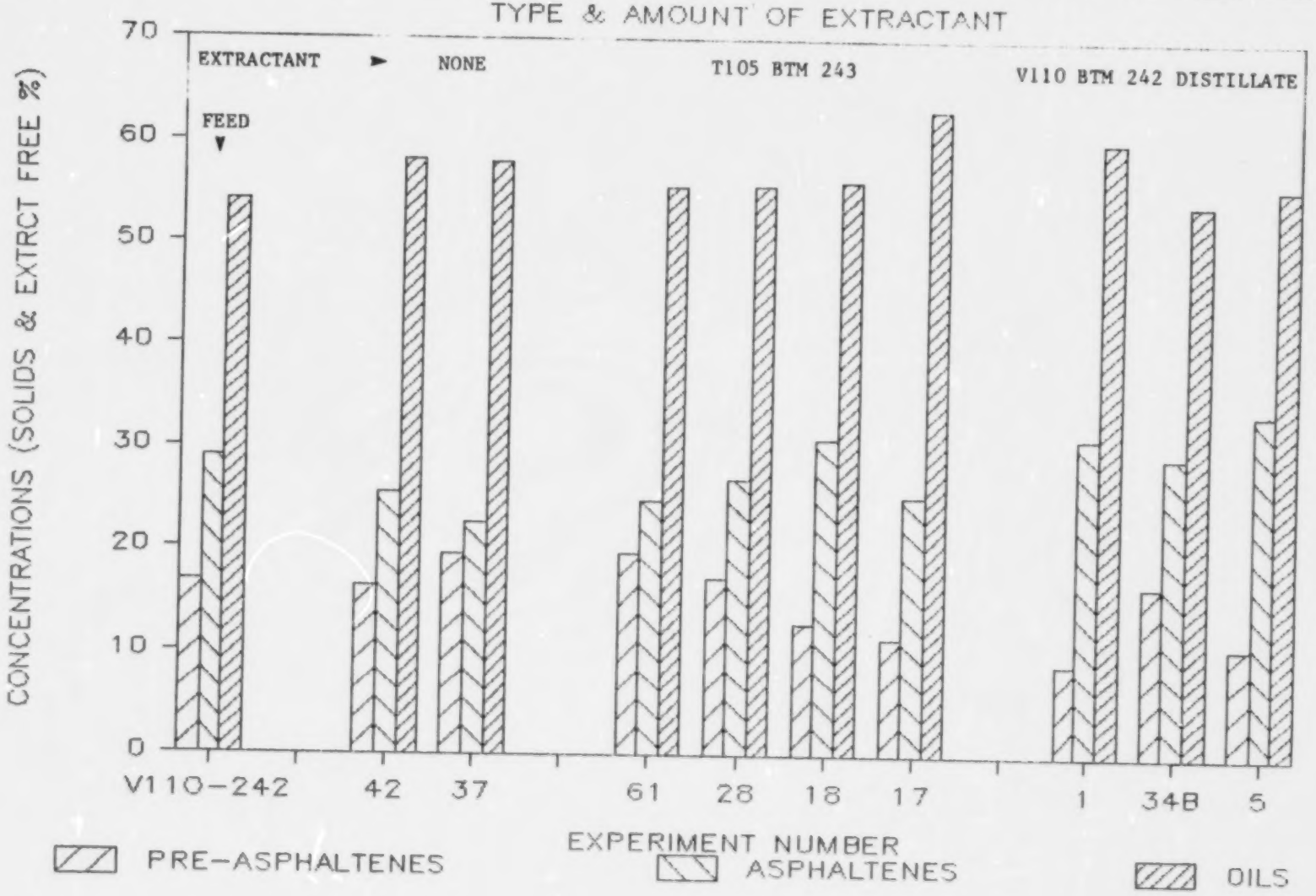
V110 BTM 242 Feed

The results for this investigation are summarized in Figure 6.6. Experiments 42 and 37 are repeat experiments which were processed without the addition of extractants. They provide an indication of the variability of the data as a result of random and development errors. Due to the relatively large variations, comparisons with regard to the extent of precipitation of the different solution components can only be made on a qualitative basis.

Similar observations as for V110 BTM 243 as feed material can be made when V110 BTM 242 is processed using a variety of extractants including T105 BTM 243 and V110 BTM 242 (IBP-500°C) distillate. It is seen that V110 BTM 242 IBP-500°C exhibits better solubility properties (Exp. 34 B and 5) with V110 BTM 242 as feed as compared to the use of T105 BTM 243 as extractant.

T105 BTM 243 shows a similar sensitivity when mixed with V110 BTM 242 as discussed in the previous sub-section for

FIG. 6.6 PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES



V110 BTM 243 in that its solubility characteristics deteriorates with the addition of increased amounts. This is illustrated by comparison of experiments 61, 28, 18, 17 and 1 which were conducted at a feed to extractant ratio range of 1:0.1 to 1:0.7.

T102 BTM 243; T102 BTM 242 Feed

In the case of T102 BTM 243 and T102 BTM 242, only few experiments were conducted since these materiasl are not expected to be used as feed materials to the Centrax Process. Figures 6.7 and 6.8 illustrate the precipitation characteristics of these feeds when mixed with different types and amounts of extractants. The limited data does not allow for definite observations but it is seen that these feeds can be separated with mimimum precipitation of either asphaltenes or pre-asphaltenes (for example, Exp. 63, 62 and 9).

Non-Processed-Derived Extractants with V110 BTM 243 as Feed

Non-process-derived extractants were also used for the processing of V110 BTM 243. The extractants used were toluene and xylene. In addition, a light fraction of T105 BTM 243 (250-300°C) was also investigated. The results are plotted in Figure 6.9.

It is seen that precipitation is not apparent at feed to extractant ratios in the range of 1:0.1 up to 1:0.2 for these extractants (experiments 69A and 71A through 71C). The same holds for process-derived extractants at these ratios. However, at feed to extractant ratio of 1:1, precipitation of pre-asphaltenes is quite significant, being greater than that experienced with any of the process-derived extractants at a 1:1 ratio.

The results of the previous three-sub-sections which dealt with type and amount of extractant in combination with different feeds can be summarized as follows:

- precipitation is a minimum when utilizing relatively small amounts of different extractants,
- precipitation may either be insignificant or very pronounced when using relatively larger amounts of extractants depending on the type of extractant used.

Temperature

The effect of processing temperature on the precipitation of the asphaltene and pre-asphaltene fractions was investigated by the processing of V110 BTM 243 with T105 BTM 243 as extractant in feed to extractant ratios of 1:0.2, 0.5, 1 and 3 at two temperature levels. These temperatures were 130°C and 180°C. The results are summarized in Figure 6.10.

FIG. 6.7 PRECIPITATION OF ASPHALTENES AND PRE–ASPALTENES

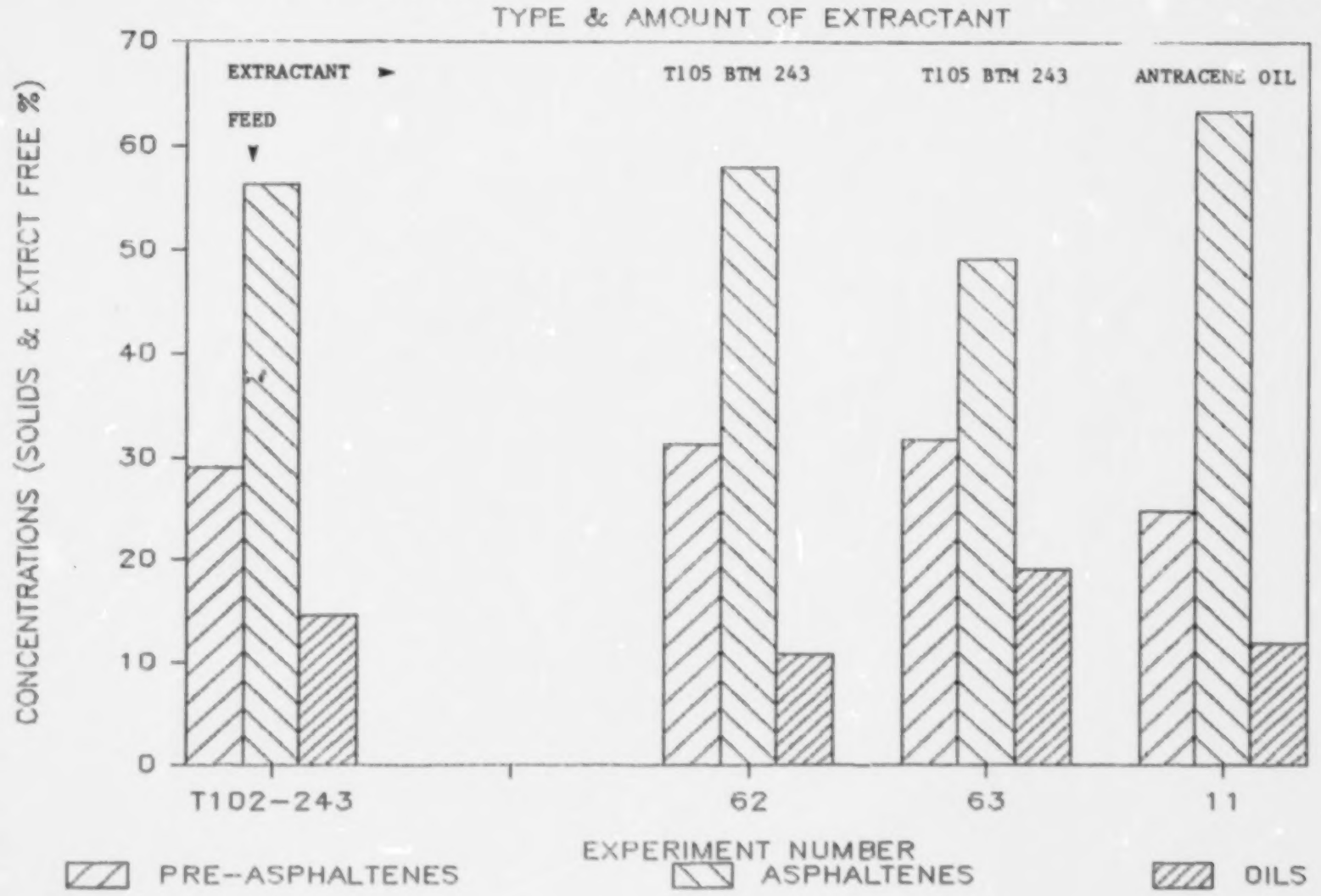


FIG. 6.8 . PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES

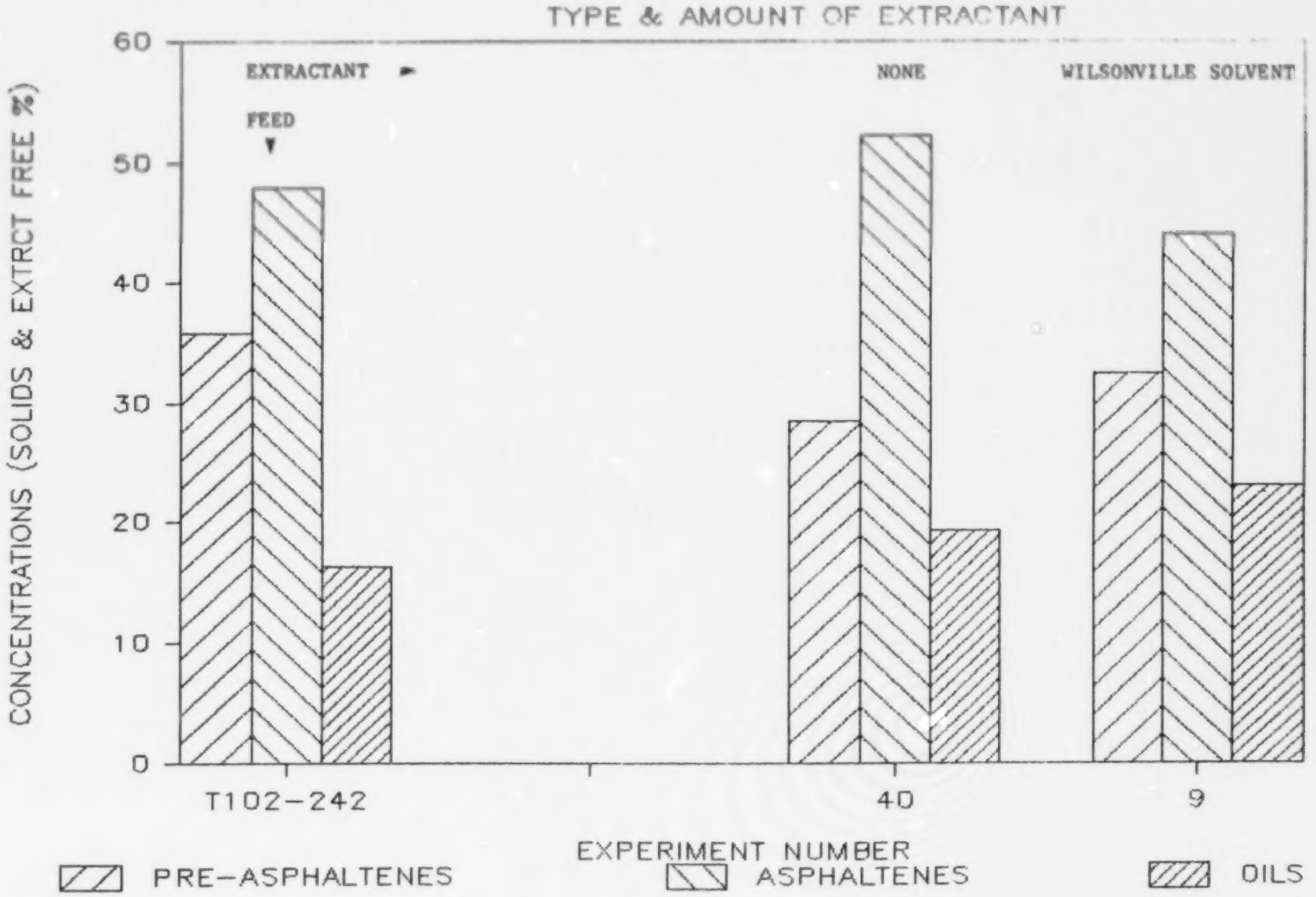


FIG. 6.9 PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES

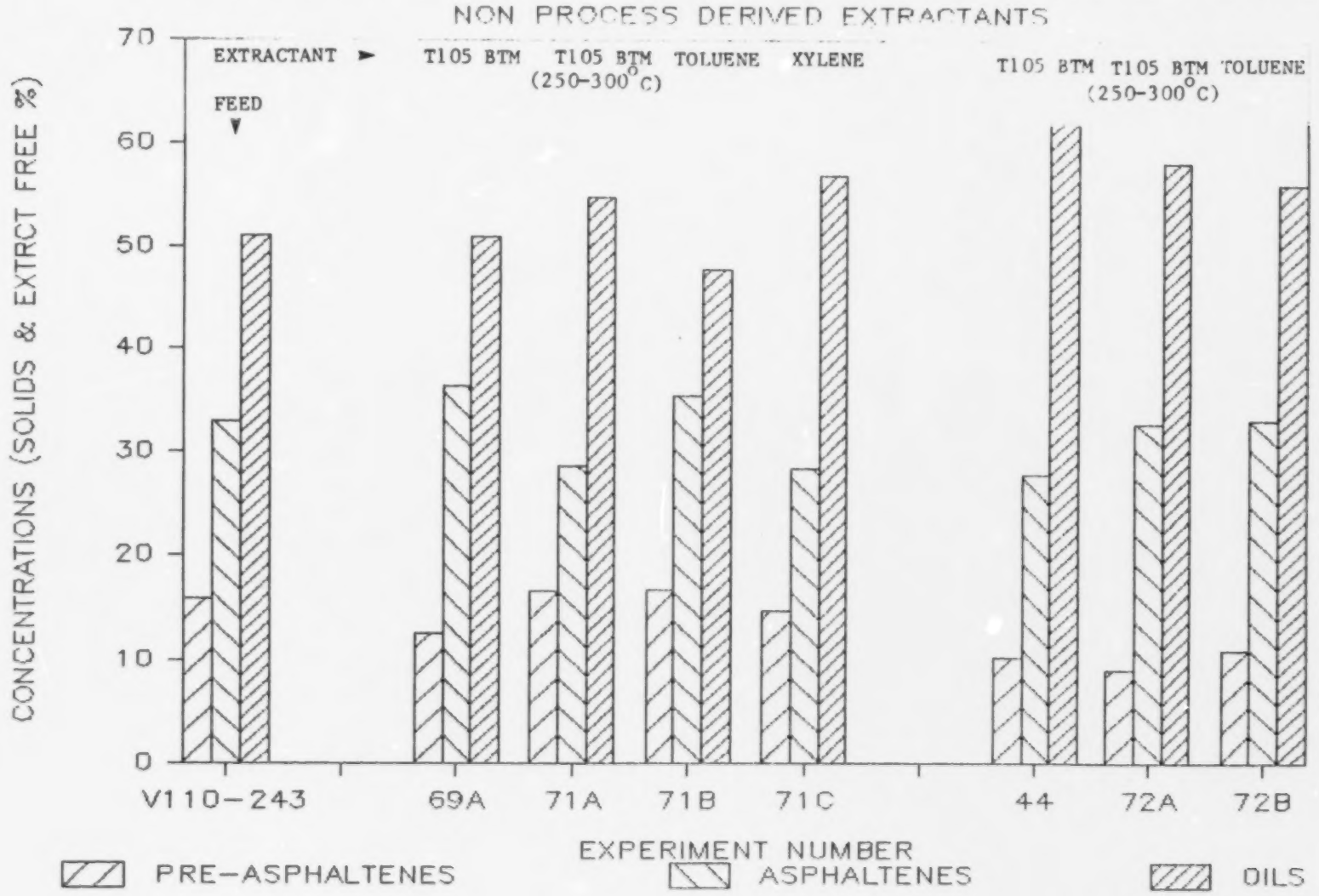
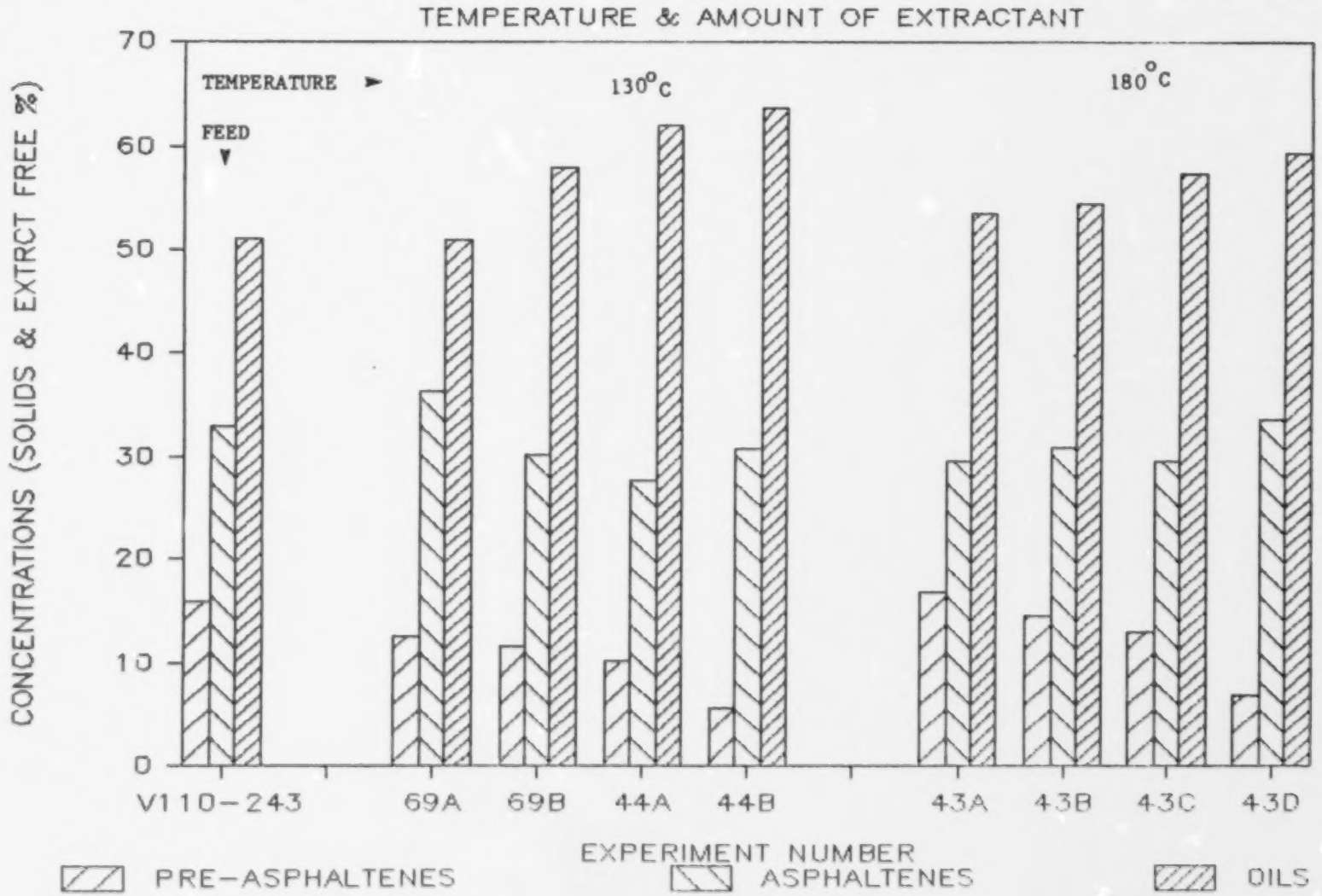


FIG. 6.10 PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES



It can be seen that processing at 130°C produces a similar trend in the amount of precipitation (Exp. 69A and B, 44A and B) with increasing amounts of extractant as that observed at 180°C. The important difference is that the increase in precipitation with higher ratios of extractant to feed is more pronounced for 130°C as for 180°C.

In short,

- precipitation is reduced when processing at higher temperatures for the particular feed and extractant mixture of V110 BTM 243 as feed and T105 BTM 243 as extractant.

Centrifugal Force

To investigate the effect of centrifugal force on precipitation, a set of experiments was conducted processing V110 BTM 243 and T105 BTM 243 in a ratio of 1:0.1, using separation forces of 1800 and 700 multiples of gravity.

The results are presented in Figure 6.11. Experiments 79A and 79C were conducted at a G force of 1800 while a G force of 700 was used in experiments 79D and 79B. Comparison between these sets of experiments conducted at 1800 and 700Gs shows that:

- no effect on precipitaiton is apparent by reducing the separation forces by a factor of 2.5.

This is as expected since centrifugal forces will not separate pre-asphaltenes and/or asphaltenes from the oil phase when they are in solution since the densities are quite similar. No promotion of precipitation is expected by the application of centrifugal forces.

Residence Time (Separation/Extraction)

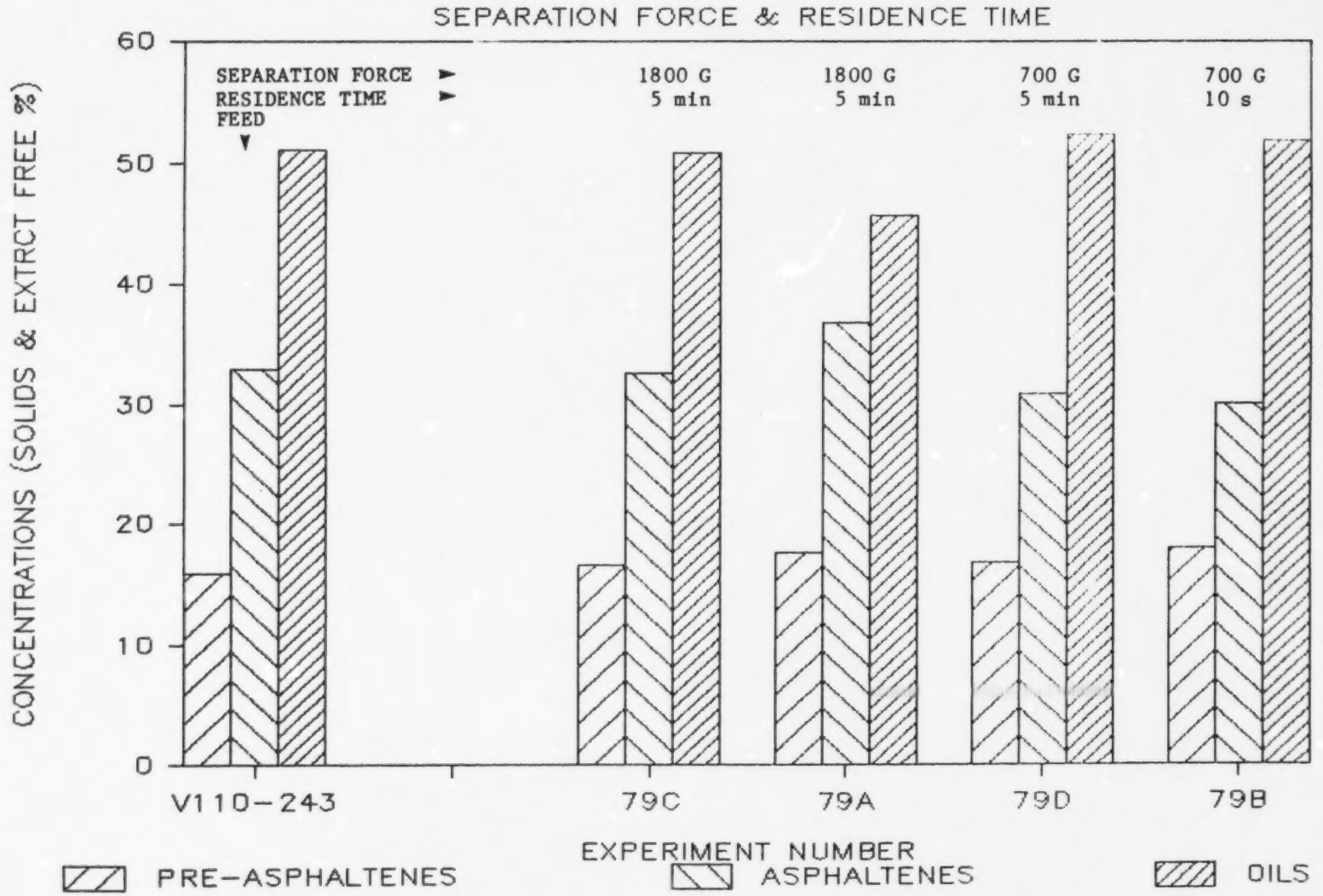
The effect of the separations residence time on precipitation was investigated in conjunction with the effects of G force (experiments 79A through 79D). This was accomplished by processing V110 BTM 243 and T105 BTM 243 in a ratio of 1:0.1 for 10 seconds and 5 minutes (Exp. 79A and 79B versus 79C and 79D respectively). The results are presented in Figure 6.11.

Comparison between 79C and 79A, and between 79D and 79B shows that:

- no effect on precipitation is visible by decreasing the residence time of the separation stage from 5 minutes down to 10 seconds.

This is as expected for the same reasons as explained in the previous sub-section.

FIG. 6.11 PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES



Residence Time (Pre-Heating Step)

To determine the effect of pre-heating residence time V110 BTM 243 and T105 BTM 243 were processed in a ratio of 1:0.2 at the maximum separation force of 1800 Gs at different levels of pre-heating residence time in combination with different values of separation residence times. The special procedure required for the rapid heating of the mixture up to the processing temperature is described in Section 6.2.1. The mixture was then separated as per Section 5.2.4. The same mixture was processed utilizing pre-heating residence times of 20 minutes and 30 seconds with separation separation/extraction residence times of 5 minutes and 10 seconds. The results are summarized in Figure 6.12.

Experimental numbers and operating conditions are related as follows:

Experiment Number	33	59A	59C	59B	59E
pre-heating residence time	20	20	20	0.5	0.5
separation residence time	5	5	0.17	5	0.17

It is seen that:

- residence time of the pre-heating step has no effect on precipitation.

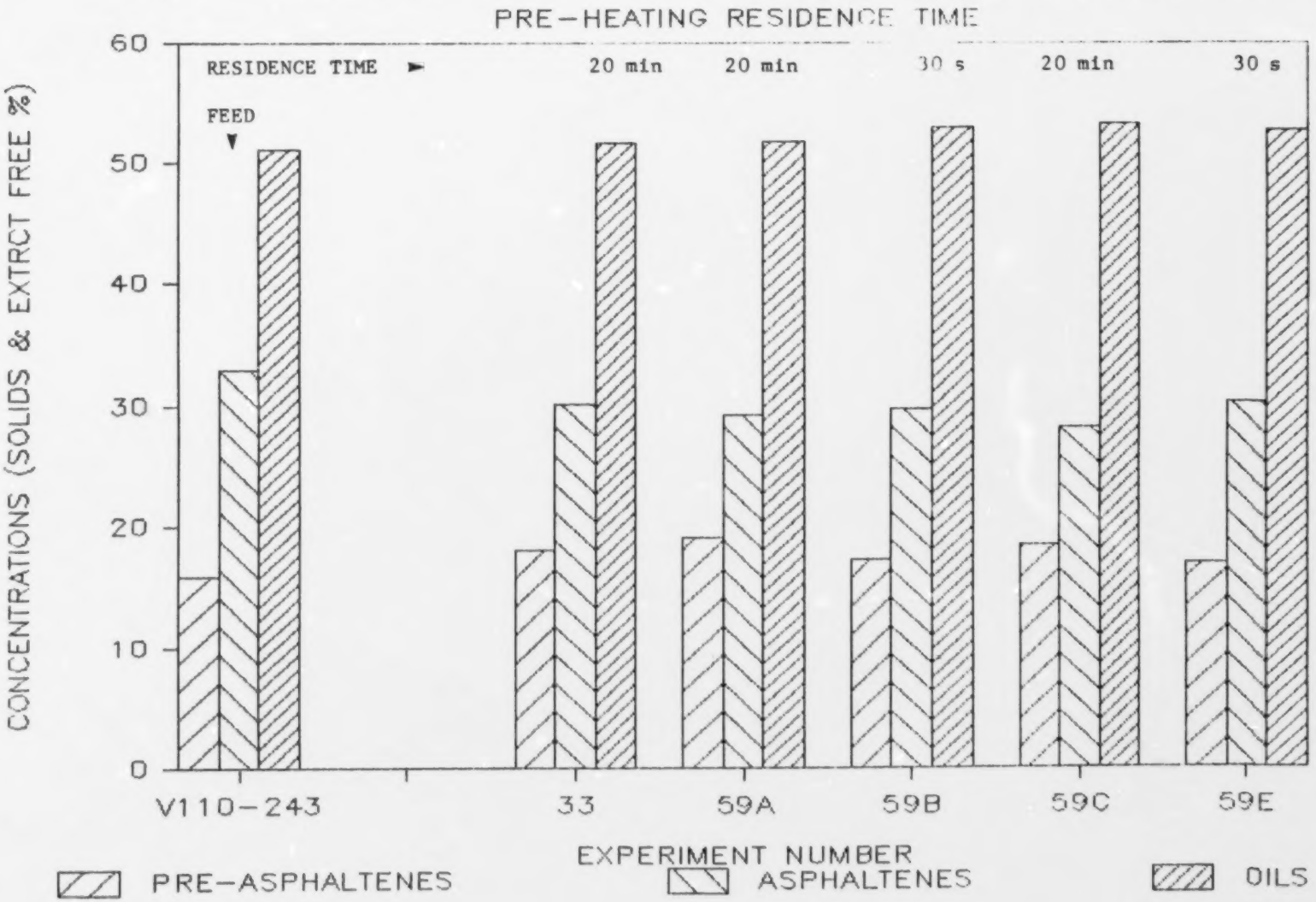
Furthermore, the above observation that the separation residence time does not affect precipitation is reconfirmed by this set of experiments since no difference is apparent between experiments 59C and 59E as compared to the other experiments in Figure 6.12. The levels of separation residence time were 10 seconds and 5 minutes respectively and as stated, appear not to have an effect on precipitation as a separate variable or have an effect as an interaction between pre-heating and separation residence times.

6.2.3 Quantitative Measure of Precipitation

Due to large variability in the determination of the THF, toluene, and the hexane insolubles, considerable scatter exists in the amounts of oils, asphaltenes and pre-asphaltenes. This is especially true of these variables are calculated from the difference of two numbers which are both subject to significant random and development errors.

For this reason, the extent of precipitation of the asphaltene and pre-asphaltene components since they are discussed in Section 6.2.2 in a qualitative manner. However, an example is provided in this

FIG. 6.12 PRECIPITATION OF ASPHALTENES AND PRE-ASPHALTENES



section of a quantitative calculation of the amount of precipitation for selected sets of experiments. Selection was based on a review of the available data and the data sets with the better consistency were used. These are experiments which were carried out in the latter stages of this work after considerable advances in the experimental and analytical techniques had been achieved. The sets of experiments so selected for numerical analysis in a quantitative manner are, 69A and B and 44A and B and 43A through D.

The ratio of oils to pre-asphaltenes (O/PA) is one quantitative indicator which can be used to calculate the extent of precipitation of pre-asphaltenes. This index of precipitation can be defined as:

$$P_{Index} \quad \frac{(O/PA) \text{ in feed (extractant and solids free)}}{(O/PA) \text{ in separated liquid (extractant and solids free)}}$$

A P_{Index} of 1.0 indicates that no precipitation of PA has occurred in the processing. The following table gives a semi-quantitative indication of the significance of the PA loss and overall loss of coal liquids during deashing.

P_{Index}	% PA Precipitated	PA Loss at 0.1 E/F Ratio	Potential loss of Coal Liquids*
1.00	0	14%	6%
1.33	25	33%	13%
2.00	50	54%	22%
4.00	75	76%	32%

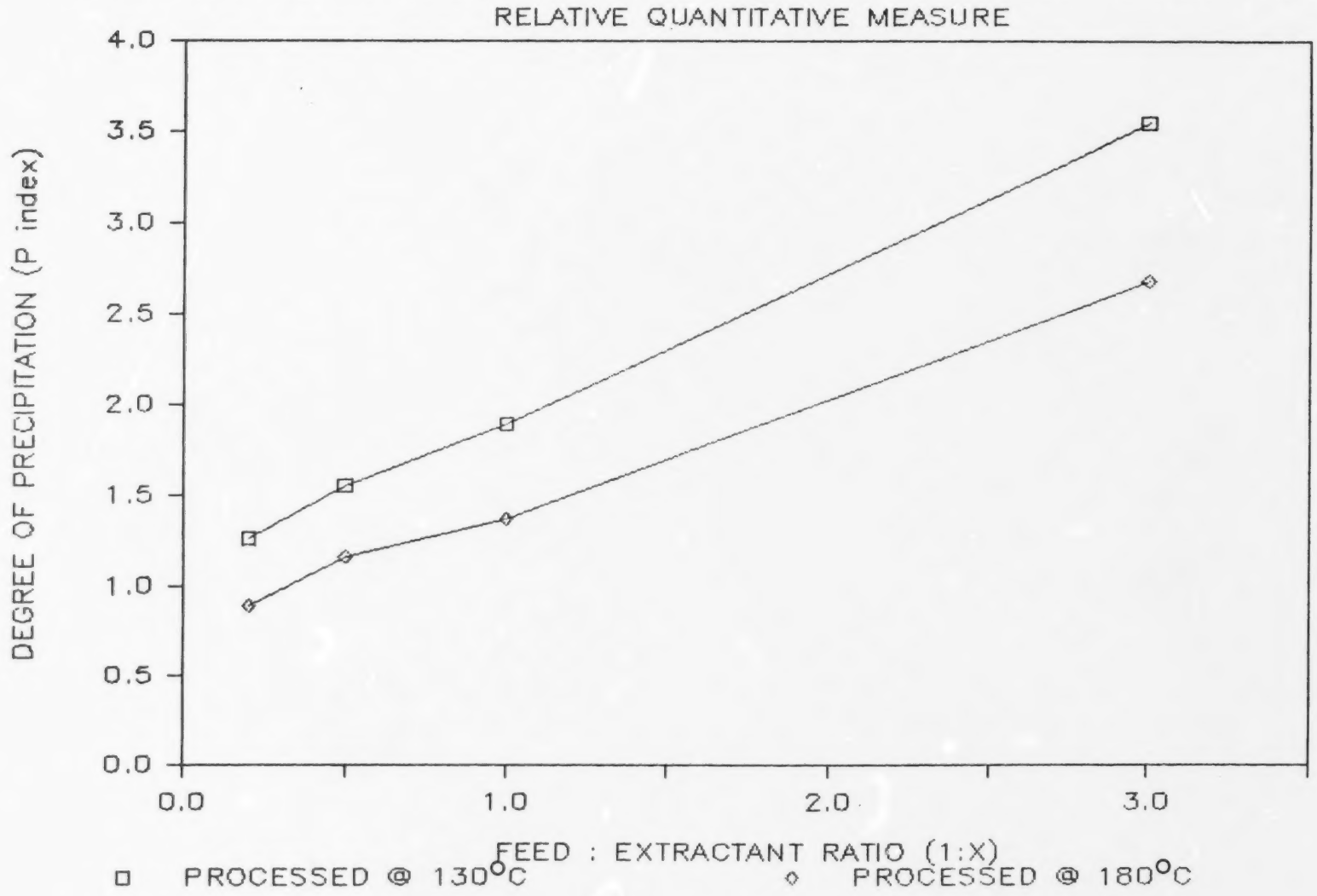
* Single Stage extraction case.

The P_{Index} is thus an indicator of the degree to which pre-asphaltenes have been precipitated which contributes to the loss of valuable coal liquefaction products.

However, it should be noted that this index does not smooth or minimize any errors associated with the data. Development of better ways of calculating amount of precipitation are required as part of future work in this area.

Application of this numerical analysis procedure to the selected sets of experiments gives the results as indicated in Figure 6.13.

FIG 6.13 PRECIPITATION OF PRE-ASPHALT.



It is seen that the amount of precipiation of pre-asphaltenes increased with increasing amounts of extractant, and further increases upon processing at lower temperatures. The same observations were made in the previous sub-section based on a qualitative analysis of the data.

6.2.4 Compressibility of Solids Phase

The compactness or compressibility of the solids phase is measured by its solids concentration. Compactness is an important variable since the more compact the solid phase is the less interstitial liquid remains. This is an important consideration with respect to the extractant recovery and overall liquid recoveries.

Listed in Table 6.5 are typical solid phase compressibilities for the solids phase of separation/extraction of V100 BTM 242, V110 BTM 243, T102 BTM 243 and T102 BTM 242.

The large variations encountered, especially for V110 BTM 242, and T102 BTM 243, are due to poor temperature control in the early experiments.

TABLE 6.5 SOLIDS PHASE COMPRESSIBILITIES

Feed Material	Extractant	Feed to Extractant Ratio	Range of Processing Temperatures (^{o}C)	Range of Compressibility (% Solids)
V110 BTM 243	V110 BTM 243 Distillate (IBP-400^{o}C)	1:0.2-1:3	180	40.03-43.66
V110 BTM 243	V110 BTM 243 Distillate (IBP-500^{o}C)	1:0.2-1:3	180	40.07-43.70
V110 BTM 243	T105 BTM 243	1:0.1-1:3	180	34.06-60.17
V110 BTM 243	T105 BTM 243	1:0.1-1:3	130	29.60-41.13
V110 BTM 242	V110 BTM 242 Distillate (IBP-500^{o}C);	1:0.3-0.67	low-180	11.20-51.22
T102 BTM 243	Anthracene Oil; T105 BTM 243	1:0.2-0.5	low-180	33.67-55.20

It was found that temperature is the dominant variable with regard to compressibility of solids. Other variables, such as type and amount of extractant have a minor effect. In general, higher processing temperatures results in more compact solids phases.

7.0 RESULTS AND DISCUSSION; MULTI-STAGE OPERATION

7.1 Counter-current Separation/Extraction

One of the multi-stage experiments was a simulated counter-current extraction. A counter-current configuration was chosen in order to simulate the expected commercial mode of operation. Counter-current operation will minimize the amount of extractant required and maximize its effect. This will provide a means of recovery of relatively large amounts of asphaltenes and pre-asphaltenes.

Since the simulation of the counter-current separation/extraction had to be conducted in batch mode at bench-scale, certain difficulties were presented by the nature of the operation. This is discussed fully in references 9 and 10. For instance, for a three stage system the simulation of stage 1 requires the liquid phase from stage 2 but in order to simulate stage 2, solids phase from stage 1 and liquid phase from stage 3 is required. Finally, to simulate stage 3, the solids phase from stage 2 is needed. Hence, an iterative approach is required.

A three stage cascade was utilized as illustrated in Figure 7.1. The stages were numbered in the direction of flow of the solids. The SL phase is the liquid that overflows from stage to stage, in a direction counter to that of the solids phase dissolving solute as it goes from stage 3 to 1. (separated liquid overflows from stage 1.) The solids phase (CS), is the stream flowing from stage 1 to 3 and leaves stage 3 concentrated in solids.

Figure 7.2 illustrates the method employed to simulate a three-stage configuration. Each circle represents a single batch separation/extraction operation and a cycle consists of three separation/extractions which approximate the three stage cascade.

Through successive cycles, the liquid and solids of each stage are approximated until steady state conditions were reached. The product streams shown on the right (CS, SL, CS, CS_3 SL_2 and SL_3) represent the final and intermediate results of the continuous scheme illustrated in Figure 7.1.

In this experiment V110 BTM 243 was used as feed with T105 BTM 243 as extractant in a feed to extractant ratio of 1:0.3. All separations were performed at 180°C under 1800 Gs centrifugal force for 5 minutes. Four cycles were performed before steady state was achieved. The results are summarized in a mass balance flow diagram as shown in Figure 7.3.

The ash concentration of the separated liquid phase was 0.08%. Mass balance calculations showed that this corresponds to an ash removal of 98.3% from the separated liquid. Theoretically, efficiencies of 100% could be attained by increasing the number of stages but the marginal gain for each added stage would be very small and impractical. Pre-asphaltene

and asphaltene recoveries were very high at 97.3%. Only 2.7% of the asphaltenes and pre-asphaltenes introduced by the feed were retained in the ash concentrate.

Shown in Figure 7.4 are the theoretical values of compositions based on flowrates of the separated liquid and compacted solids phase attained during the experiment. These theoretical values were based on the following assumptions: no precipitation of asphaltenes and pre-asphaltenes during processing, constant flows of solids phase and liquid phase (i.e., the operating line is of constant slope) and complete separation of solids at each stage. Figure 7.4 shows that for this 3-stage operation, 99.8% of the asphaltenes and pre-asphaltenes can theoretically be recovered. From this analysis it can be seen that the actual process approaches theoretical values. The counter-current configuration appears to be a viable process arrangement.

FIG 7.1 SCHEMATIC FLOW DIAGRAM OF THREE STAGE COUNTER-CURRENT EXTRACTION

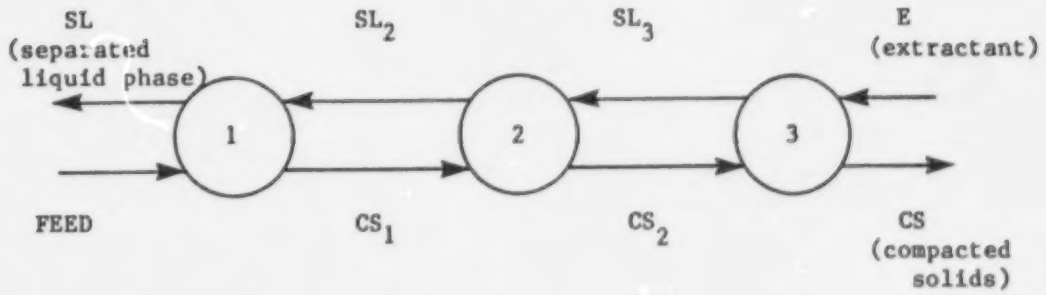


FIG. 7.2 COUNTER-CURRENT SIMULATION EXPERIMENTS

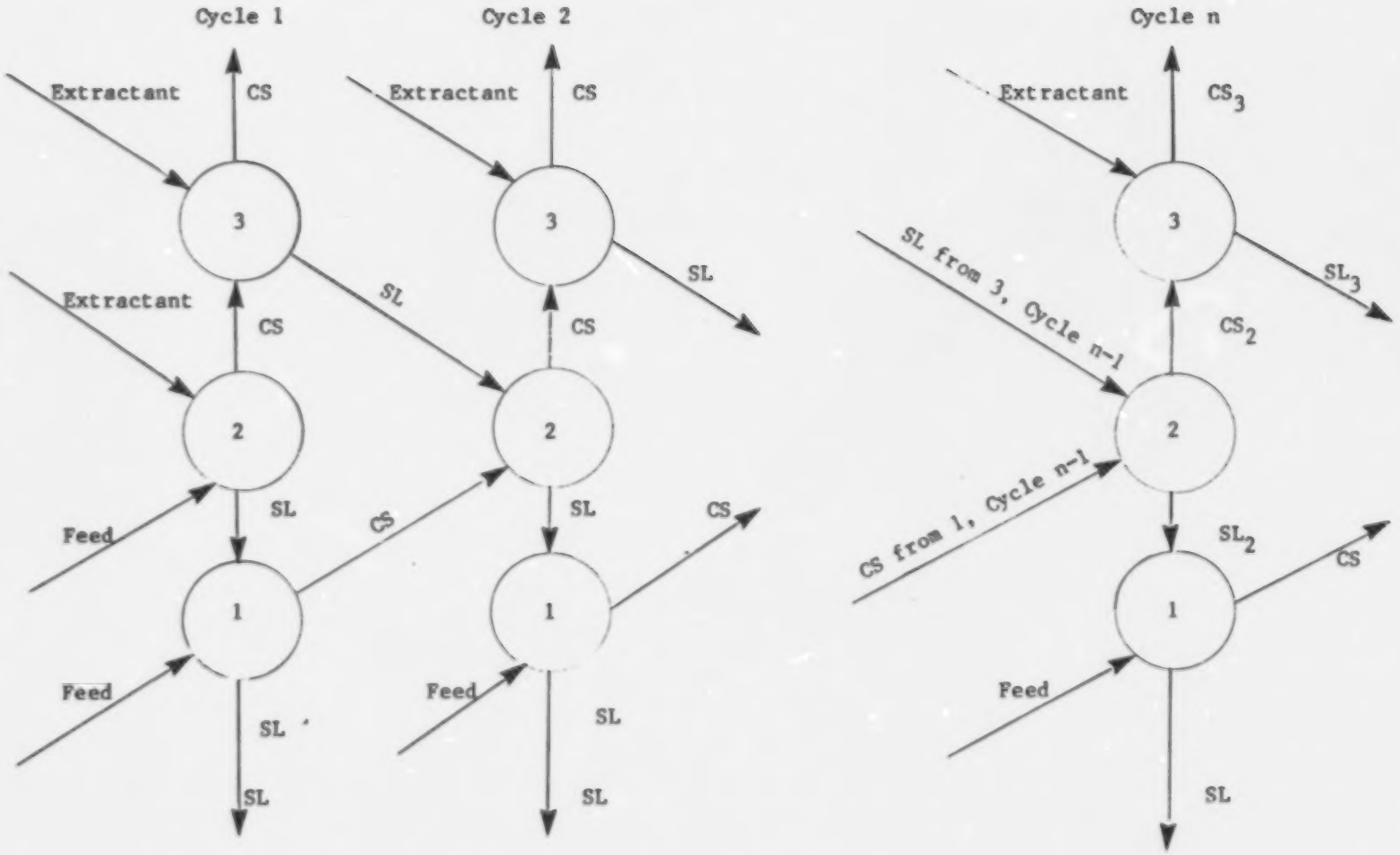


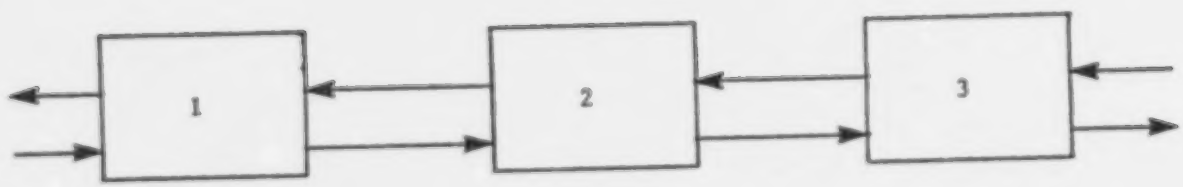
FIG. 7.3 SIMULATED COUNTER-CURRENT SEPARATION/EXTRACTION RESULTS

SL	
O	67.83
A & PA	46.09
UC	0.29
Ash	0.08
	113.51

SL_2

SL_3

E	
O	29.94
A & PA	0.00
UC	0.00
Ash	0.00
	29.94



CS_1

CS_2

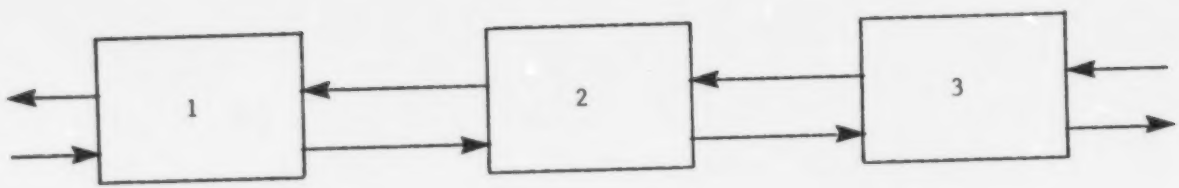
FEED (V110 BTM 243)	
O	50.46
A & PA	40.67
UC	4.64
Ash	4.24
	100.00

CS	
O	7.98
A & PA	1.11
UC	2.85
Ash	3.89
	15.83

FIG. 7.4 THEORETICAL COUNTER-CURRENT SEPARATION/EXTRACTION

SL	
O	72.91
A & PA	40.60
UC	0.00
Ash	0.00
	113.51

E	
O	29.94
A & PA	0.00
UC	0.00
Ash	0.00
	29.94



SL_2

SL_3

CS_1

CS_2

FEED (V110 BTM 243)	
O	50.46
A & PA	40.67
UC	4.64
Ash	4.24
	100.00

CS	
O	6.88
A & PA	0.07
UC	4.64
Ash	4.24
	15.83

7.2 Cross-Current Separation/Extraction

Another of the multi-stage experiments performed simulated a three-stage cross-current configuration.

Cross-current processing may be a possible commercial scale configuration. This type of operation will probably result in fewer stages for a comparable asphaltene and pre-asphaltene recovery than possible with a counter-current arrangement. This makes for a less complex process arrangement plus allows for greater process flexibility such as, use of different types and amounts of extractants at each stage.

Cross-current multi-stage separation/extraction is an extension of the single-stage separation/extraction discussed in Section 6.2. In this configuration the solids phase is successively contacted with fresh extractants shown in Figure 7.5 for the case of three stage operation. Three concentrated liquid phases and a single concentrated solids phase result.

In this experiment V110 BTM 243 was used as feed with T105 BTM 243 as extractant in a feed to extractant ratio of 1:0.3 for the first stage. The separations/extractions were conducted at a maximum centrifugal force for 5 minutes at a temperature of 175-180°C. Each stage consisted of a single preparation and separation/extraction step as outlined in Section 5.2. Approximately equal amounts of extractants were added in each stage and the three liquid overflows were kept separated and analyzed.

Figure 7.6 presents the results in the form of a mass balance flow diagram. In addition, a theoretical mass balance flow diagram, Figure 7.7 has been calculated using flow rates from this experiment and based on the assumptions that no precipitation occurs throughout the processing sequence and complete solids separation at each stage. As can be seen, actual concentrations of the liquid overflows (SL_1, SL_2, and SL_3) approach those of the approximated theoretical concentrations. It appears that 97.0% of the asphaltenes and pre-asphaltenes are recovered in these streams.

The asphaltene and pre-asphaltene recoveries produced, indicate that precipitation is at a minimum and cross-current operation is an effective method of separating this material.

FIG. 7.5 SCHEMATIC FLOW DIAGRAM OF THREE-STAGE CROSS-CURRENT EXTRACTION/SEPARTION

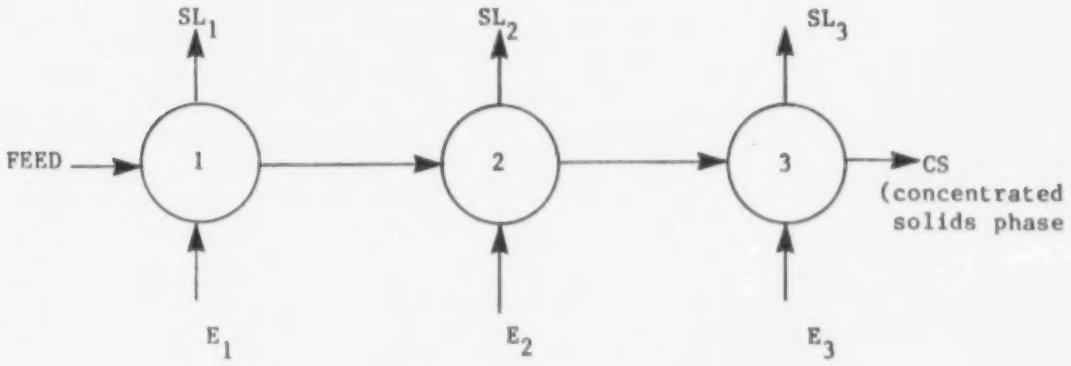


FIG. 7.6 MASS BALANCE FLOW DIAGRAM - CROSS-CURRENT SEPARATION/EXTRACTION ACTUAL

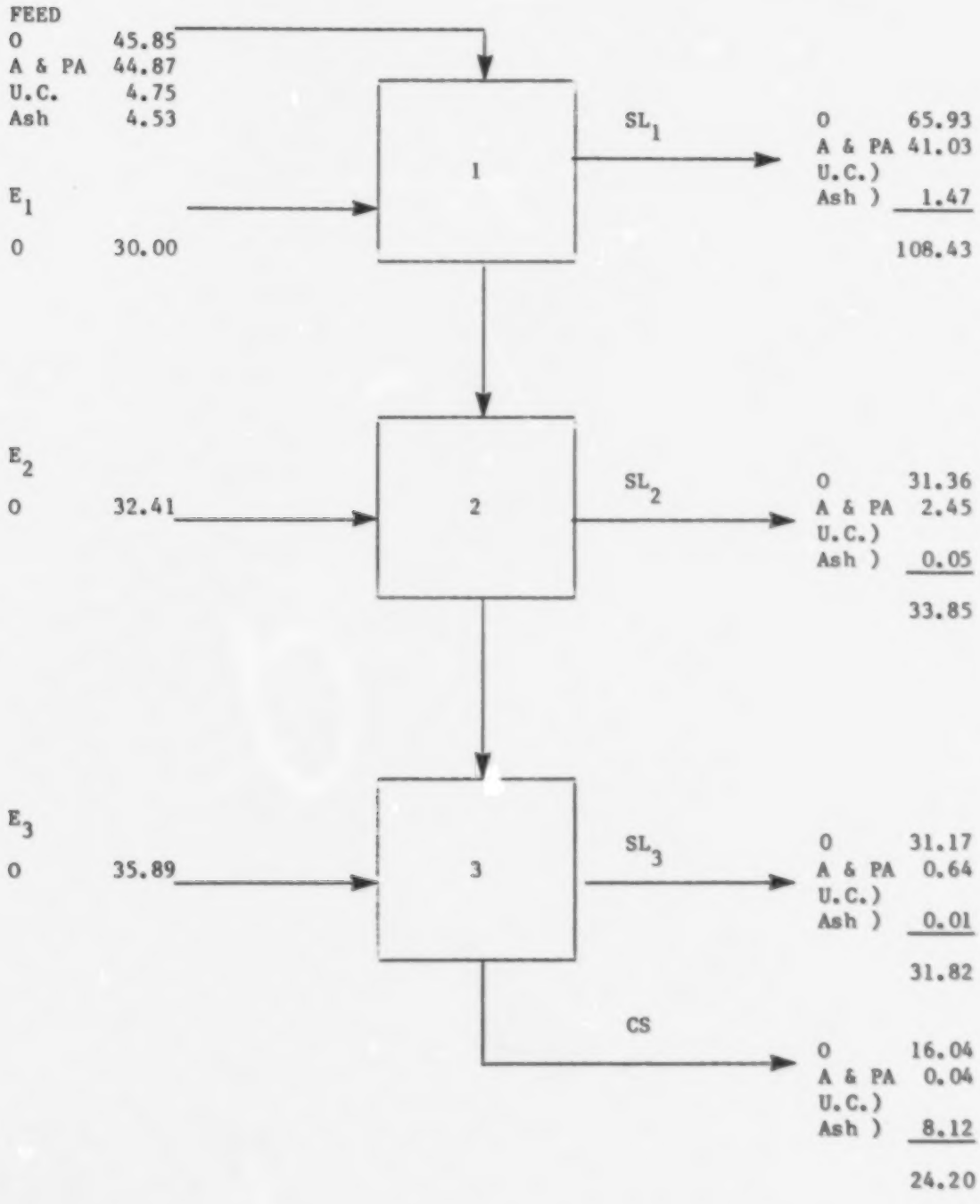
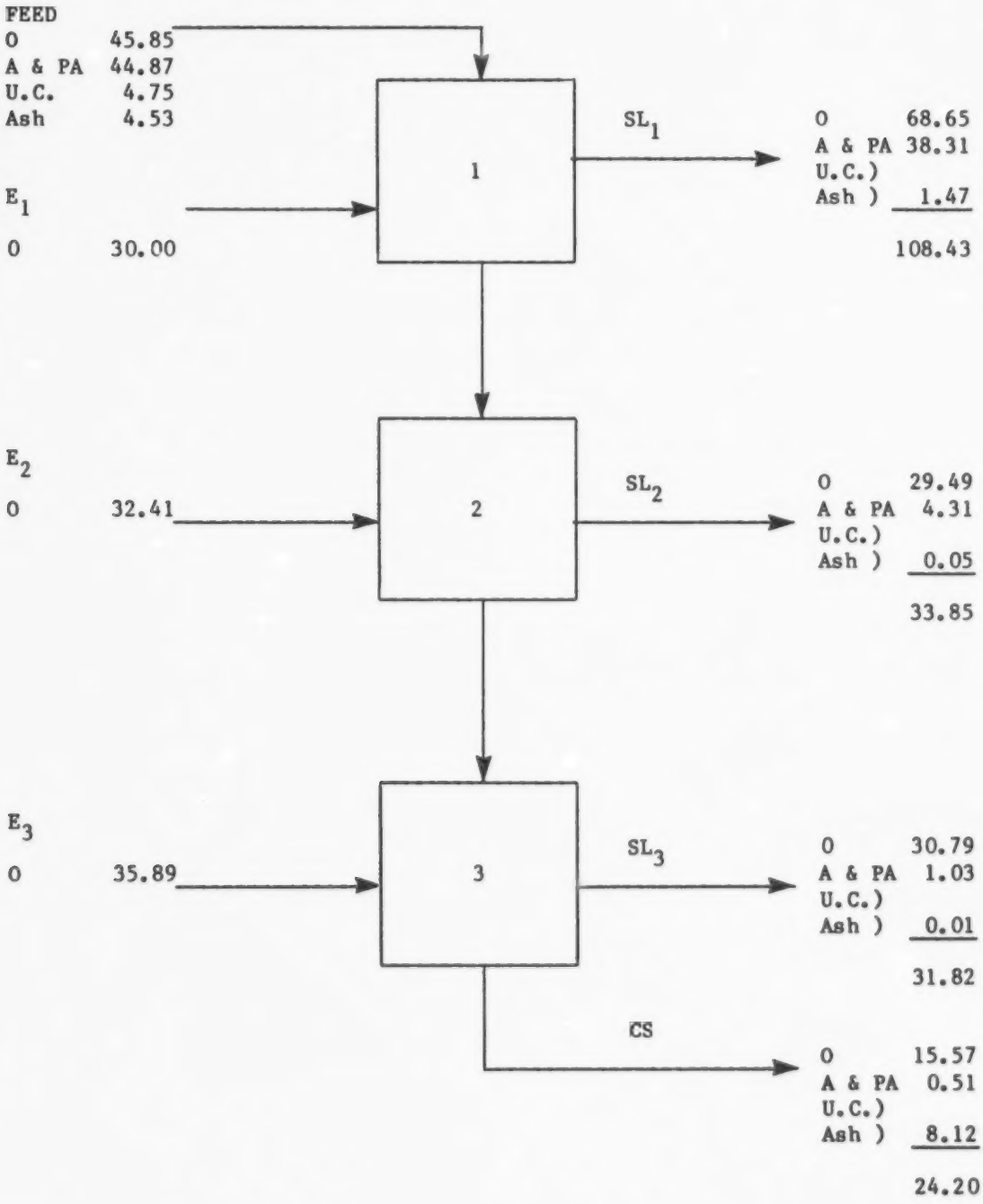


FIG. 7.7 MASS BALANCE FLOW DIAGRAM - CROSS-CURRENT SEPARATION/EXTRACTION THEORETICAL



7.3 Extractant Recovery

The final stage of the process is the quantitative recovery of the extractant through the use of flash evaporation techniques previously described in Section 5.2.

A large number of recoveries were carried out which were part of the development program. As described in Sect 3.2.5, this development was centered in processing and apparatus improvements.

Since it is a high temperature process(500^{o}C), thermal degradation of organic liquids can occur. The results of stability investigation are summarized in Secion 4.3.3.

The results of trouble-free experiments are listed in Table 7.1 for the feed materials V110 BTM 242 and V110 BTM 243. The overall product recovery is defined as

$$PR = \left(100 - \frac{\text{Total Solids in AC} - \text{Total Solids in Feed}}{\text{Total Feed} - \text{Total Solids in Feed}} \right)$$

Losses shown in mass balance column are assumed to be gases such as, methane, ethane, etc., which were produced but not collected. Losses in the overall product recovery column are believed to be materials that are converted into solid coke material or gaseous material. If the mass balances are 100%, then all overall product losses can be assumed to be due to production of coke.

The results show:

- the ash and unconverted coal is concentrated in a product that is 100% THF insoluble,
- overall product recoveries of 100% are attainable,
- production of light gases is minimized,
- production of coke is minimized,
- ash can be classified as dry and friable.

The results indicate that little, if any, pre-asphaltene and asphaltene components are recovered during this stage but are instead converted into THF insoluble material.

The optimum conditions yield maximum insoluble material in the ash concentrate, maximum recovery of liquids from the feed and minimal gaseous products. The investigation of temperatures suggests high temperatures and further work will produce a temperature range closer to the optimum. This optimum processing temperature will result in no coke or gas production.

TABLE 7.1 EXTRACTANT RECOVERY FROM ASH CONCENTRATE - SUMMARY*

Starting Material	Mass Balance %	Gas Produced %	Coke Produced %	Overall Product Recovered %	THF Insol. Fraction of Ash Concentrate %	Description of Ash Concentrate %
V110 BTM 243 T105 BTM 243	95.7	4.3	0	100.2	100	Dry friable
V110 BTM 242 T105 BTM 242	100	0	10.5	89.5	100	"
V110 BTM 242 T105 BTM 243	94.6	5.4	0	100.0	100	"

* Tests conducted at 550°C Plate Temperature.

8.0 INTEGRATION OF THE CENTRAX SEPARATION PROCESS INTO THE TWO-STAGE WILSONVILLE COAL LIQUEFACTION PROCESS

8.1 Process Configurations

8.1.1 Type of Liquefaction Product

Appended to this report are process flowsheets of the Wilsonville SRC and HTR units reproduced from reference (14). These flowsheets have been included for convenience in locating the process location of samples used in this study. They are found in Appendix 2.

Separation/extraction of V110 BTM material is discussed exclusively here, although it is just as feasible to start with T102 BTM material. It can be separated by similar process configurations as discussed below. However, first indications are that the amount of required extractant is larger as compared to that required for V110 BTM. In addition, use of V110 stream directly eliminates the requirements for the T102 vacuum column and the subsequent recombination of thermal distillate and separated product. In case this thermal separation step is desirable, it can be incorporated either before or after the Centrax separation process.

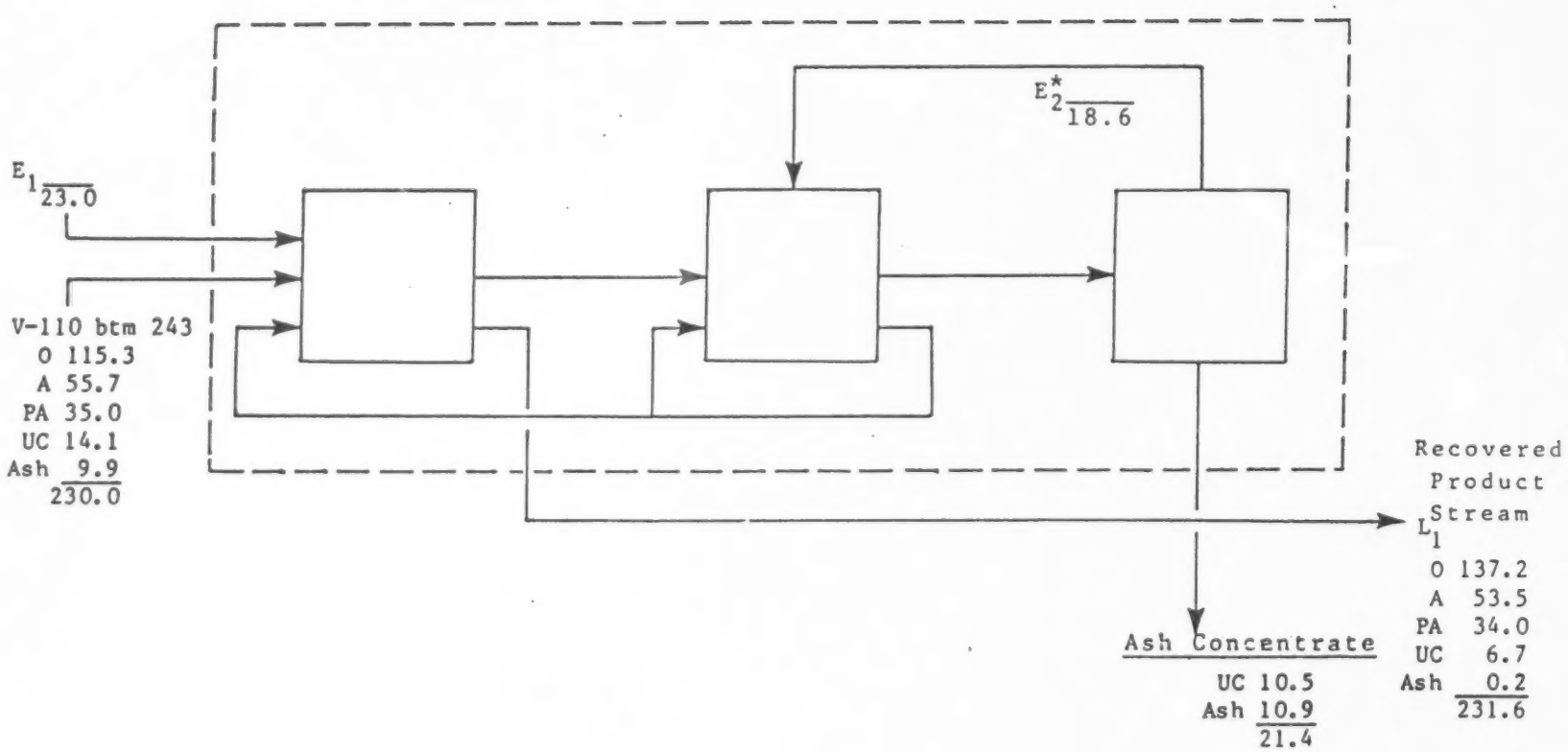
8.1.2. Process Configurations and Material Balances

Material balance flow diagrams are shown in Figures 8.1, 8.2, and 8.3. These configurations are some of the possible process lay-outs. Better definition of the best configuration will be obtained after progression to a continuous pilot scale operation as compared to the present batch scale laboratory simulation work. The separation and product recovery obtained on the laboratory scale are a correct indication of the expected performance on a larger scale, since the values of most of the key process variables which govern the separation and extraction will, in all probability, not significantly change in scale-up.

The material balances are normalized on a total mass basis. Total mass balances required small adjustments due to evaporation of some of the lighter components during processing. The numbers are scaled to the same relative values (100 units of MF (moisture-free) coal feed to the ITSL process) as shown in the material flow diagrams of the technical progress reports of EPRI for Runs 242 and 243 (12,13). This allows for direct comparison between the figures of this report and those from EPRI. The values for the individual components are obtained by analysis as described previously.

Figure 8.1 shows a particular process configuration which uses as part of the extracting liquid, material derived within the Centrax process, denoted by E_2. Figure 8.2 shows a material balance for separation/recovery of the same V110 BTM 243 which uses all external

FIG. 8.1 CENTRAX MATERIAL BALANCE FLOW DIAGRAM
RUN 243 PROCESS SCHEME I



NOTES

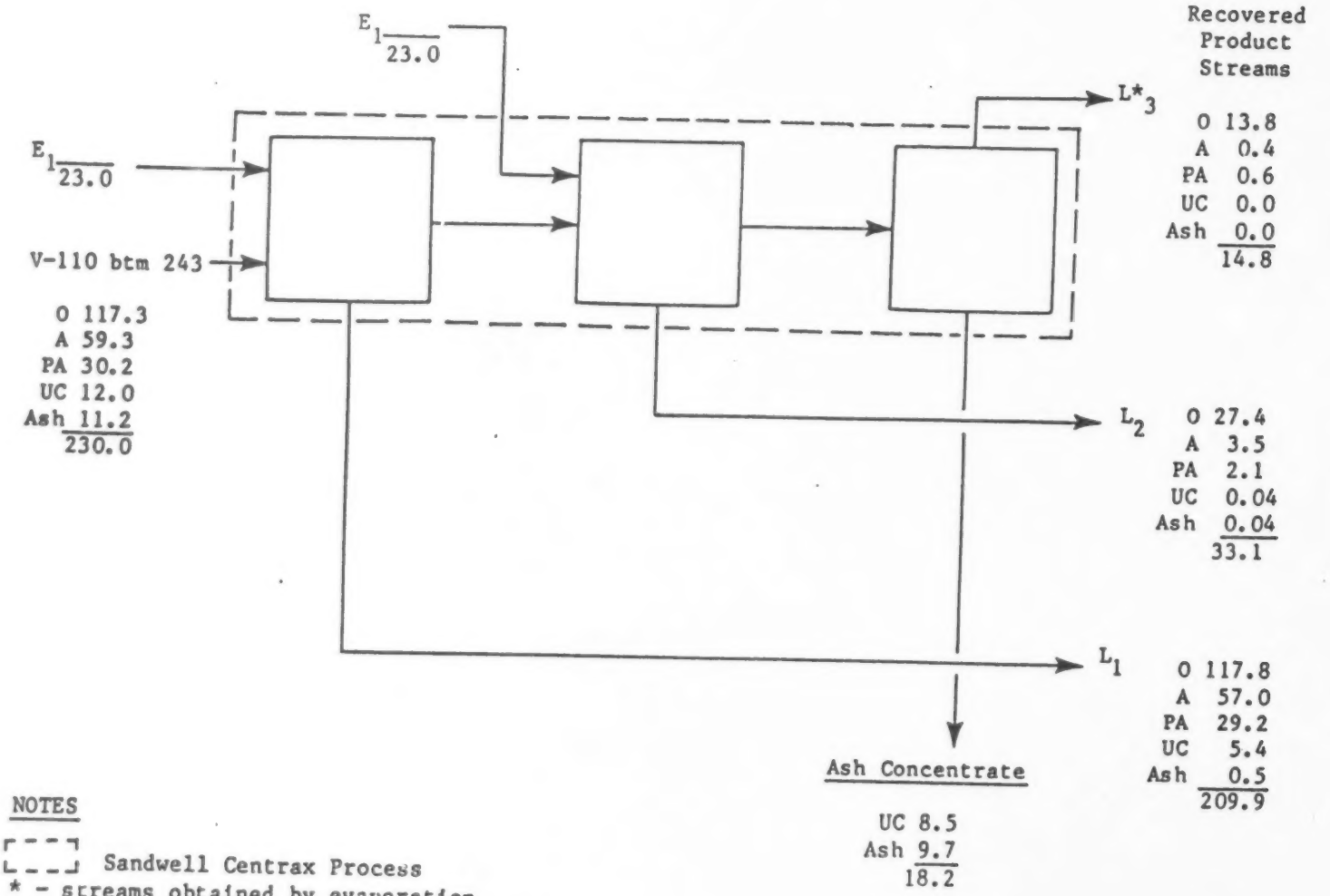
┌ ─ ─ ┐
└ ─ ─ ┘ Sandwell Centrax Process

* - streams obtained by evaporation

Units are scaled to 100 units of MF coal feed to the ITSL process

E - extractant

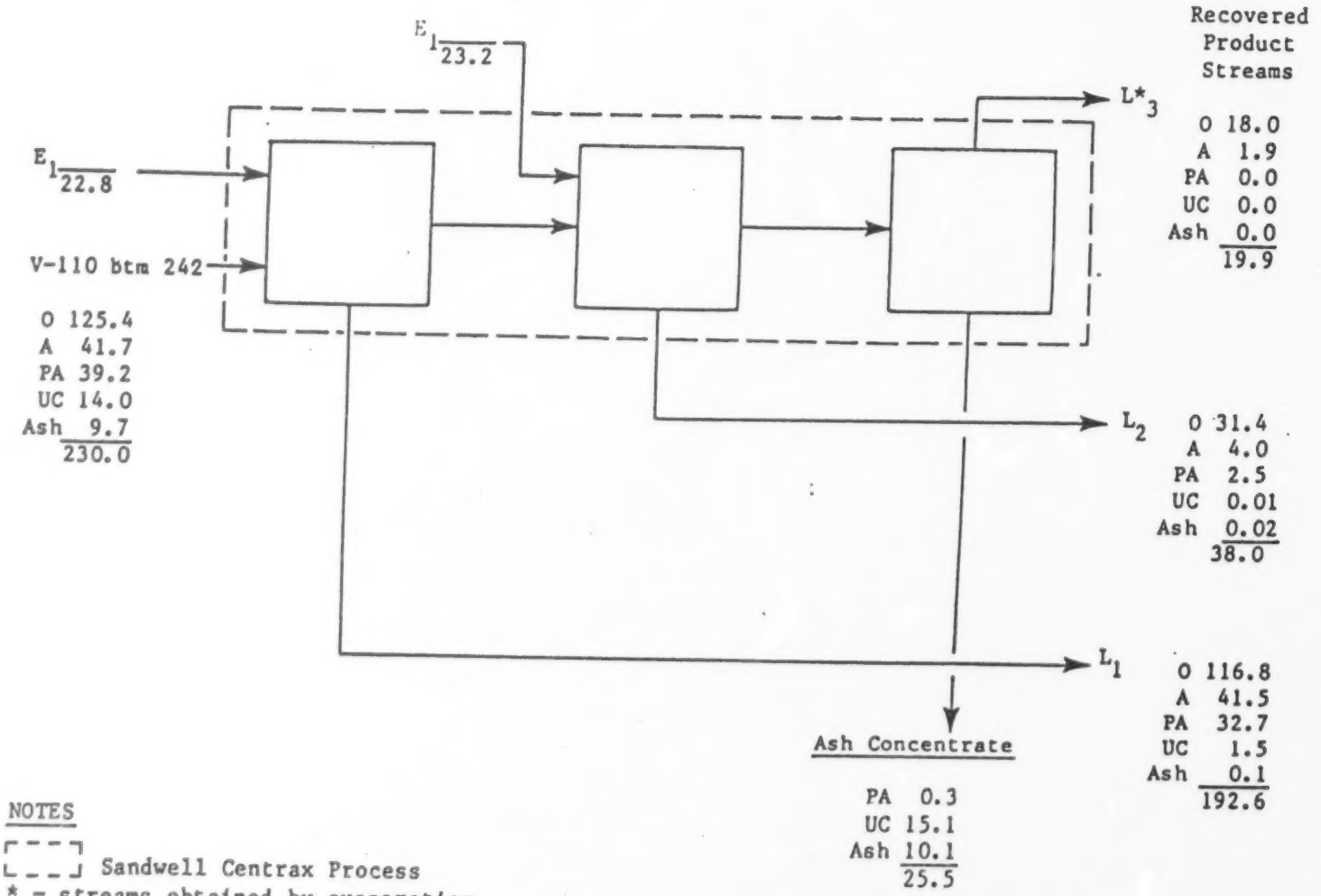
FIG. 8.2 CENTRAX MATERIAL BALANCE FLOW DIAGRAM
RUN 243 PROCESS SCHEME II



NOTES

Sandwell Centrax Process
* - streams obtained by evaporation
Units are scaled to 100 units of MF feed coal to the ITSL process
E - extractant

FIG. 8.3 CENTRAX MATERIAL BALANCE FLOW DIAGRAM
RUN 242 PROCESS SCHEME II



NOTES

Sandwell Centrax Process

* - streams obtained by evaporation

Units scaled to 100 units of MF feed coal to the ITSL process

E - extractant

derived extractant (E_1). E_1 stands for the bottom material of T105 BTM 243. This same material was used to separate/recover V110 BTM 242 coal liquefaction product. The results of which are shown in Figure 8.3.

Comparison between the use of all external extractant (Figure 8.2) and use of partial external extractant (Figure 8.1) shows that within experimental error the same recovery of product is obtained. That is, the ash concentrate values are approximately equal, and the main product stream from the separation processes (L_1) are of similar composition. The all external extractant process configuration produces two extra product streams. These may be used directly in other parts of the liquefaction process, such as, for instance for recycle solvent, or they may be processed further. Streams L_1 and L_2 may be concentrated with regard to their asphaltene and pre-asphaltene content if required either by evaporation or by the use of an anti-solvent. Overall liquefaction process economics will dictate the different choices.

Separating/recovering of V110 BTM material from runs 242 and 243 with the same extractant from run 243 results in slightly different recoveries as shown in Figures 8.3 and 8.2 respectively. Slightly less of the material of run 242 is recovered. This appears to be a consequence of a minimal 'mis-match' between the properties of the run 243 derived extractant and the liquefied product of run 242. Run 242 derived extractant was not available for this work. This effect might be beneficial in case it is desired to 'reject' some of the pre-asphaltene type of materials. If on the other hand, a market exists for this product directly or indirectly by upgrading its rejection can be minimized.

8.2 Expected Process Performance

8.2.1. Recovery Efficiency

Calculation of the recovery efficiency is confounded by the appparent aging of the processed samples. This is most notable by the material denoted as pre-asphaltene shown in Table 4.1.3. This table shows the effect of aging between original Wilsonville analysis and sample analysis in Sandwell's laboratory approximately 8 months later as described in Section 4.2. The table also illustrates the effect of solvents used to define the compositions into the fractions oil, asphaltenes and pre-asphaltenes. However, recoveries can still be calculated on an absolute basis by comparison of the different amounts in the feed versus those in the extracted fractions, and compared to recoveries obtained, in for instance, Wilsonville Run 243. This allows for a valid comparison in spite of the difference in composition of the feed material.

From the material balances (Figures 8.1, 8.2, and 8.3), and from reported data (14) the recoveries are calculated and listed in Table 8.1.

TABLE 8.1 PERCENT PRODUCT RECOVERY COMPARISONS

Component	Centrax			Wilsonville
	Run 243		Run 242	Run 243 G
	Process Scheme 1	Process Scheme 11	Process Scheme 11	CSD* Process
Oils	99.2	97.4	97.0	97.3
Asphaltenes	96.0	102.7	113.7	97.11
Pre-asphaltenes	97.1	105.6	89.8	16.8
Total 'Liquids'	98.1	99.6	98.6	92.0

* CSD - Critical Solvent Deashing

Table 8.1 presents the recovered fractions of each of the components and of the sum of the three components which is defined as 'total liquids'. The total "liquid" recoveries reported above, are based on direct weight measurements. The recoveries of the components are based on and defined by the solubility properties of the components in specific solvents and as such, are subject to greater relative error than the total liquid measurements. The recoveries greater than 100% are probably due to these relative errors, and not the result of retrogressive reactions in the Centrax process. The difference with regard to percent recovery, as defined here, between the Centrax and CSD processes is that the latter recovers much less pre-asphaltenes. In terms of net products from the coal liquefaction process, the difference between 92 and 99% recovery of total liquid results in an actual increase in net liquid product of between 15 and 20%.

8.2.2 Energy Rejection in Ash Concentrate

Energy rejection is a term used to describe the heating value lost to the ash concentrate as a fraction of the feed coal heating value. It is made up of material which is not converted in the liquefaction reactor and of material which is not separated in the recovery/separation process.

Estimating that the heating value of the ash concentrate is approximately 13,700 Btu/lbm moisture-ash free (MAF), and that of the feed coal is approximately 12,700 Btu/lbm MAF (11,14), then the energy rejection is:

a) 10 - 13% for the run 243 tests, and
b) 18% for the run 242 test,

where the 18% is a non-optimized value. No effort has been made up to now to decrease the total amount of ash concentrate for tests on run 242 material. This relative high value of 18 percent is due to a small 'mis-match' of extractant properties to the properties of V110 BTM 242.

The energy rejected in the Centrax ash concentrate is in the form of only unconverted coal. This confirms the high recovery of all liquid components in the Centrax process. This residue is dry, friable material which can be easily crushed and transported

8.2.3 Effect of the Centrax Process on the ITSL Process Operation

Separation/recovery is effected exclusively with process streams from the ITSL process without the requirement of special preparatory processing. The extractant used for the examples presented here is T105 BTM. Other extractants can be used if required. V110 BTM are used as feed to the separation process. It appears to be 'more' suitable than T102 BTM, although the latter can also be separated. More extractant is probably required in that case. Use of V110 BTM has as advantage that it may eliminate the T102 vacuum evaporation step and the subsequent recombination of thermal distillate and recovered product. Stream L_1, Figures 8.1, 8.2, 8.3, can be fed directly into the hydrotreater or it can be pre-processed if required. Some of the oils may be removed by atmospheric evaporation if it is feasible to feed a more concentrated stream in asphaltenes and pre-asphaltenes to the hydrotreater. Most of the pre-asphaltenes and part of the asphaltenes may for instance be separated from stream L_1 by an anti-solvent process to precipitate selectively the 'heavier' fraction. Part of these components could also be removed by vacuum evaporation of a bleed stream from L_1. Streams L_2 and L_3 can possibly be used as recycle solvent or be upgraded. Thus the Centrax process recovers the liquefaction product from the ash and unconverted coal material without effecting either the upstream or downstream process units with possible elimination of some of the ITSL process unit operations.

9.0 PRELIMINARY ESTIMATE OF THE ENERGY REQUIREMENTS FOR OPERATION OF THE CENTRAX PROCESS

Separation is carried out at atmospheric pressure and, for these process materials, at approximately 170°C. Extractant recovery from the solids is at present effected by flash evaporation at atmosheric pressure. Thus the sources of energy consumption are:

a) heat losses from the process,
b) required power for driving of the separators,
c) specific and latent heat of evaporation for extractant recovery from the solids,
d) specific and latent heat of evaporation for extractant recovery from the recovered liquid product, and
e) mechanical energy for movement of the process materials

If it is assumed that the liquid product stream L_2, Figures 8.2 and 8.3, is used as recycle solvent then the energy requirements for all three process configurations are approximately equal. Neglecting heat losses, specific heat, and non-centrifugal mechanical energy requirements as a first approximation, energy consumption can be estimated as follows:

basis:
- heating value of coal Illinois #6 MF — 11,500 Btu/lbm (12)
- heat of vaporization of extractant — 125 Btu/lbm (11)
- mechanical separation factor — 3,000 G

then the approximate energy requirements as a percentage of the heating value of the feed coal are :

1) heat of vaporization:

$$125 \frac{\text{Btu}}{\text{lbm}} \times (23 - 18)\ \text{lbm} \times \frac{1}{100\ \text{lbm}} \times \frac{1}{11500} \frac{\text{lbm}}{\text{Btu}} \times F_1 \times 100\% = 0.9\%$$

where:
- 23 is the relative amount of used extractant,
- 18 is the relative amount of extractant separated from the ash concentrate by evaporation,
- 100 is the relative amount of MF coal feed, and
- F_1 is an estimated inefficiency factor estimated to be 2.

2) power for mechanical separation:

$$1.88 \frac{\text{Btu}}{\text{lbm}} \times (253 - 80)\ \text{lbm} \times \frac{1}{100\ \text{lbm}} \times \frac{1}{11500} \frac{\text{lbm}}{\text{Btu}} \times F_2 \times F_3 \times 100\% = 0.5\%$$

where:- 1.88 Btu/lbm is the theoretical kinetic energy requirement based on a certain basket diameter and the 3000 G specification,

- F_2 is an estimate of the inefficiency for a centrifugal separation device, estimated to be 3.

- F_3 is a conversion or inefficiency factor for fossil to electric energy usually 3.

It is to be noted that the 0.5% will probably decrease on scale up since centrifugal separation becomes more efficient for larger feed capacities. The value for the centrifugal device efficiency is for a relatively small to intermediate sized unit. From this analysis on energy requirements it follows that for this separation process the dominating variable is the amount of used extractant. Energy recovery schemes have not been taken into account for this preliminary estimate. They could possibly further reduce the energy requirements.

On the basis of a preliminary estimate of the energy requirements, the Centrax Process will consume around 1.5% of the energy in the feed. Compared to the significantly greater value in extra product recovered by the Centrax Process 10-15%, the energy demand of the process is not of great importance. In any event, the Centrax Process would also replace other processing units in the liquefaction process to the extent that the Centrax energy demand is offset by these other savings.

10.0 NOTATION

IBP	:	Initial Boiling Point. As determined by gas chromatography, it is the point at which a cummulative area count equal to 0.5 percent of the total area under the chromatogram is obtained.
SL	:	Separated Liquid
CS	:	Compacted Solids
AC	:	Ash Concentrate
E	:	Extractant
F	:	Feed
THF	:	Tetrahydrofuran
O	:	Oil
PA	:	Pre-Asphaltenes
A	:	Asphaltenes
A & PA	:	Sum of Asphaltenes and Pre-Asphaltenes
S	:	Solids
UC	:	Unconverted Coal
P_{Index}	:	Measure of the Precipitation of Pre-Asphaltenes
PR	:	Overall Product Recovery

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APPENDIX 1

EXPERIMENTAL OPERATING CONDITIONS

EXPERIMENTAL OPERATING CONDITIONS

EXP.	STARTING MATERIALS		PREPARATION		SEPARATION/EXTRACTION				
#	Feed	Extractant	Ratio	Temp. (°C)	τ_p min.	Pressure	Force of Separation (multiples of gravity)	τ_s min.	Temp. (°C)
1	V110 242	T105 243	1:0.67	150	30	Atm.	1800	5	∠150
2	V110 242	none		200					∠200
4	V110 242	WV	1:1	160					∠160
5	V110 242	V110 242 distill 500°C	1:1	160					90+
6	V110 242	V110 242 distill 500°C + THF	1:1.2	160					∠160
7	T102 242	V110 242 distill 500°C	1:3	150					70+
8	T102 242	V110 242 distill 500°C	1:3	150					105-130
9	T102 242	WV	1:2	200					110-130
11	T102 243	AO	1:3	200					120-130
12	V110 243	AO	1:2	200					120-130
13	V110 243	V110 242 distill 500°C	1:0.5	200					160
14	V110 243	T105-243	1:0.3	200					150-160
15	V110 243	T105-243	1:1.5	180			no separation		
17	V110 242	T105 243	1:0.3	180	30	Atm.	1800	5	150-160
18	V110 242	T105 243	1:0.3	180					150-160
19	V110 243	T105 243	1:3	180					150-160
20	V110 243	T105 243	1:0.2	180					150-160
21	V110 243	T105 243	1:0.25	180	60				150-160
26	V110 243	none		180	20				160-170
27	V110 243	T105 243	1:0.3	180					160-170
28	V110 242	T105 243	1:0.3	180					160-170
30	T102 243	none		180					170
31	T102 243	T105 243	1:0.5	200					170-180
32	V110 243	T105 243	1:0.3	180					160-170
33	V110 243	T105 243	1:0.2	180					160-170
34a	V110 243	V110 243 distill 500°C	1:0.3	180					160-170
34b	V110 242	V110 242 distill 500°C	1:0.3	180					160-170
37	V110 242	none		180					170
39	V110 243	none		180					170
40	T102 242	none		200					180-185
41	V110 243	none		180					170
42	V110 242	none		180					170
43a	V110 243	T105 243	1:3	180					175-180
43b	"	"	1:1	180					175-180
43c	"	"	1:0.5	180					175-180
43d	"	"	1:0.2	180					175-180
44	V110 243	T105 243	1:1	135					135-140
45a	V110 243	V110 243 distill 500°C	1:0.2	180					175-180
45b	"	"	1:0.5	180					175-180
45c	"	"	1:1.0	180					175-180
45d	"	"	1:3	180					175-180
46a	V110 243	V110 243 distill 400°C	1:0.2	180					175-180
46b	"	"	1:0.5	180					175-180
46c	"	"	1:1.0	180					175-180
46d	"	"	1:3	180					175-180
59a	V110 243	T105 243	1:0.2	180					175-180
59b	V110 243	T105 243	1:0.2	180	0.5				175-180
59c	V110 243	T105 243	1:0.2	180	20			0.17	175-180
59d	V110 243	T105 243	1:0.2	180	20			0.17	175-180
59e	V110 243	T105 243	1:0.2	180	0.5			0.17	175-180
61	V110 242	T105 243	1:0.1	180	20			5	175-180
62	T102 243	T105 243	1:0.2	200					185
63	T102 243	T105 243	1:0.4	200					185
64	V110 243	T105 243	1:0.3	150					150
65	V110 243 *	T105 243(250-300°C)	1:0.3	100					90-95
67	V110 243 *	T105 243(250-300°C)	1:0.3	100					90-95
68	V110 243	T105 243	1:0.3	180					175-180
69a	V110 243	T105 243	1:0.2	130					130-135
69b	V110 243	T105 243	1:0.5	130					130-135
71a	V110 243	T105 243(250-300°C)	1:0.1	140					140
71b	V110 243	Toluene	1:0.1	120					120
71c	V110 243	Xylene	1:0.1	120					120
72a	V110 243	T105 243(250-300°C)	1:1	140					140
72b	V110 243	Toluene	1:1	110					110-120
72c	V110 243	T105 243(250-300°C)	1:1	140					140
79a	V110 243	T105 243	1:0.1	180			1800	0.17	175-180
79b	V110 243	T105 243	1:0.1	180			700	0.17	175-180
79c	V110 243	T105 243	1:0.1	180			1800	5	175-180
79d	V110 243	T105 243	1:0.1	180			700	5	175-180

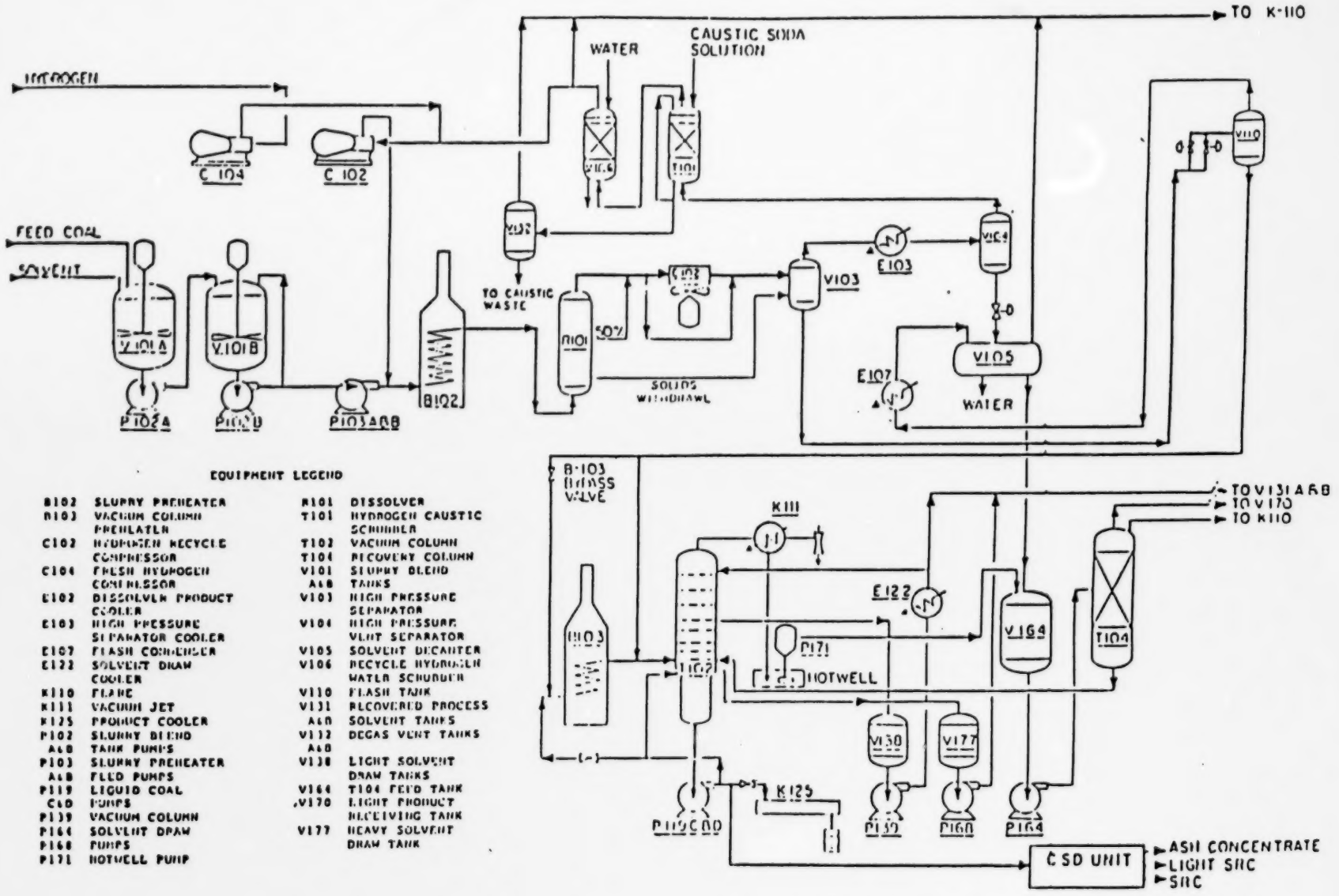
LEGEND

AO Anthracene Oil
WV Wilsonville solvent
τ_s Residence time - separation/extraction
τ_p Residence time - preparation
* Pre-Asphaltene-free

APPENDIX 2

SRC UNIT FLOWSHEET

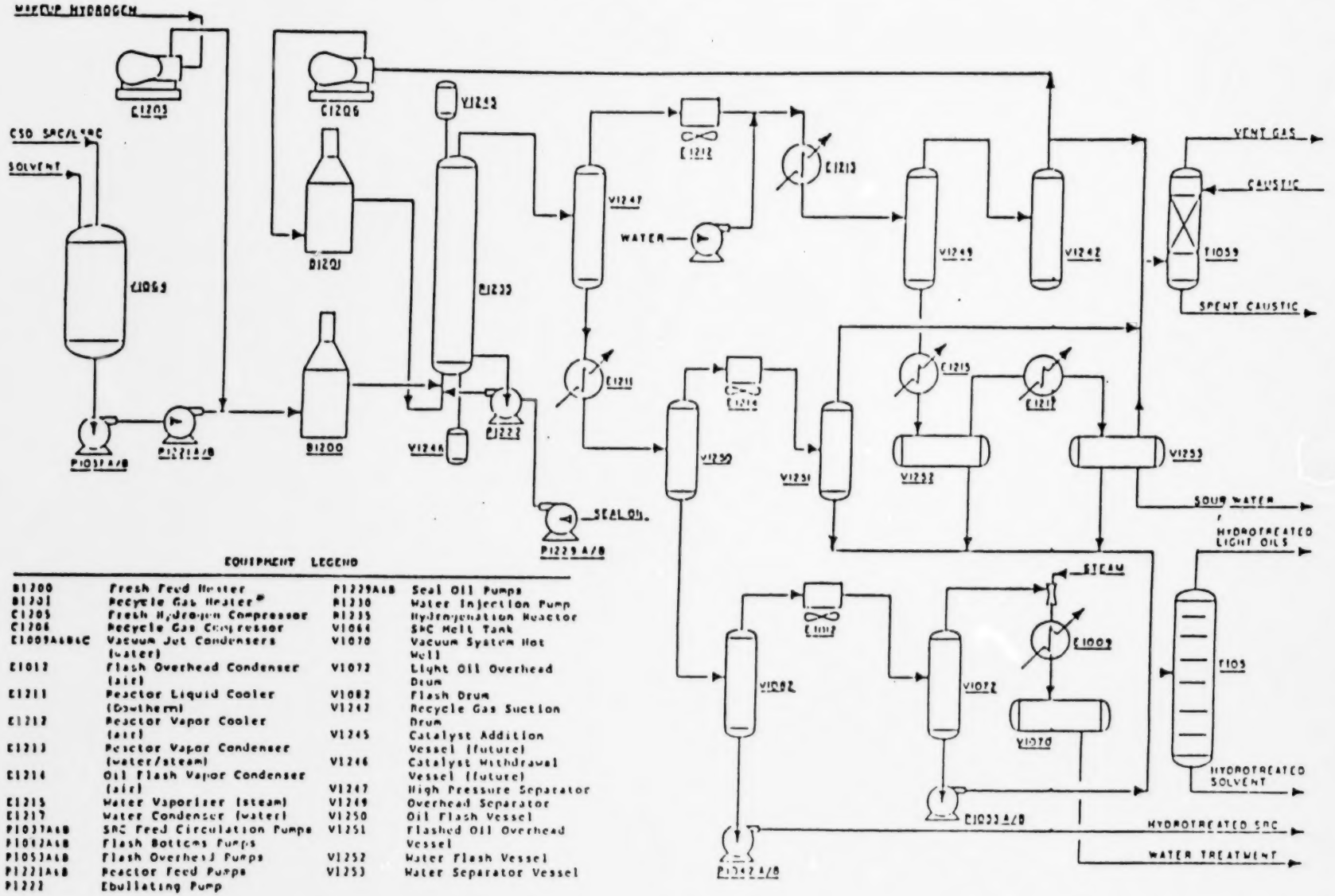
HTR UNIT FLOWSHEET



EQUIPMENT LEGEND

B102	SLURRY PREHEATER	R101	DISSOLVER
B103	VACUUM COLUMN PREHEATER	T101	HYDROGEN CAUSTIC SCRUBBER
C102	HYDROGEN RECYCLE COMPRESSOR	T102	VACUUM COLUMN
C104	FRESH HYDROGEN COMPRESSOR	T104	RECOVERY COLUMN
E102	DISSOLVER PRODUCT COOLER	V101	SLURRY BLEND TANKS A&B
E103	HIGH PRESSURE SEPARATOR COOLER	V103	HIGH PRESSURE SEPARATOR
E107	FLASH CONDENSER	V104	HIGH PRESSURE VENT SEPARATOR
E122	SOLVENT DRAW COOLER	V105	SOLVENT DECANTER
K110	FLARE	V106	RECYCLE HYDROGEN WATER SCRUBBER
K111	VACUUM JET	V110	FLASH TANK
K125	PRODUCT COOLER	V131	RECOVERED PROCESS SOLVENT TANKS A&B
P102	SLURRY BLEND TANK PUMPS A&B	V132	DEGAS VENT TANKS A&B
P103	SLURRY PREHEATER FEED PUMPS A&B	V138	LIGHT SOLVENT DRAW TANKS
P119	LIQUID COAL PUMPS C&D	V164	T104 FEED TANK
P139	VACUUM COLUMN	V170	LIGHT PRODUCT RECEIVING TANK
P164	SOLVENT DRAW PUMPS	V177	HEAVY SOLVENT DRAW TANK
P168			
P171	HOTWELL PUMP		

SRC UNIT FLOWSHEET (Reproduced from reference (14))



EQUIPMENT LEGEND

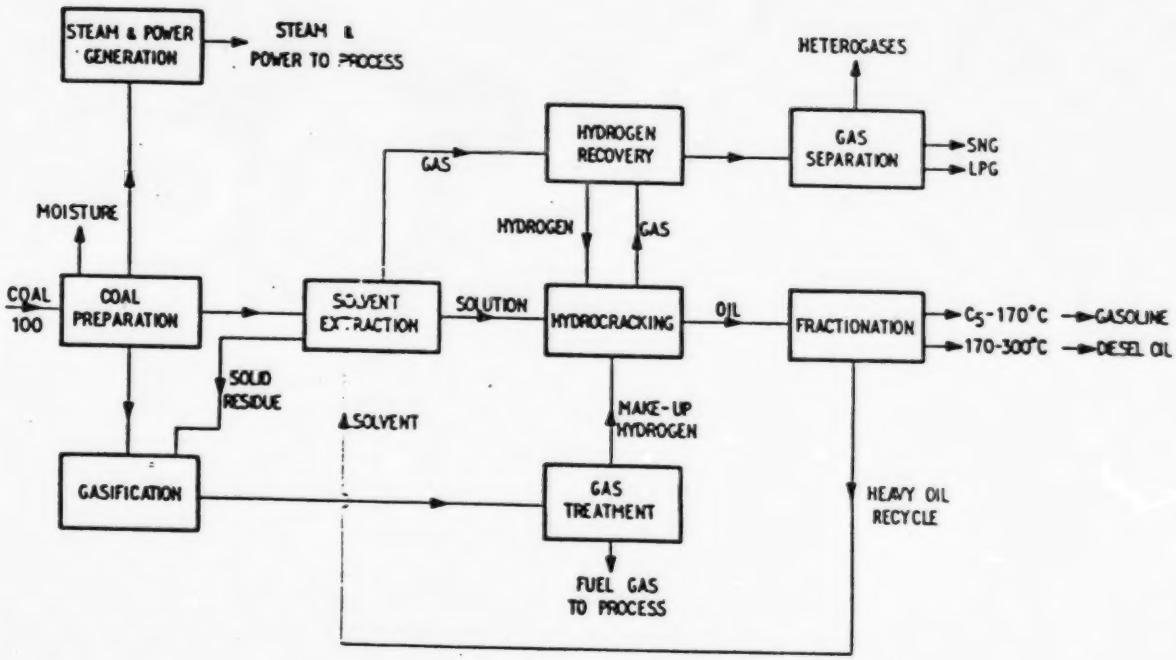
B1200	Fresh Feed Heater	P1229A&B	Seal Oil Pumps
B1201	Recycle Gas Heater*	P1230	Water Injection Pump
C1205	Fresh Hydrogen Compressor	R1235	Hydrogenation Reactor
C1206	Recycle Gas Compressor	V1064	SRC Melt Tank
E1009A&B&C	Vacuum Jet Condensers (water)	V1070	Vacuum System Hot Well
E1012	Flash Overhead Condenser (air)	V1072	Light Oil Overhead Drum
E1211	Reactor Liquid Cooler (Dowtherm)	V1082	Flash Drum
E1212	Reactor Vapor Cooler (air)	V1242	Recycle Gas Suction Drum
E1213	Reactor Vapor Condenser (water/steam)	V1245	Catalyst Addition Vessel (future)
E1214	Oil Flash Vapor Condenser (air)	V1246	Catalyst Withdrawal Vessel (future)
E1215	Water Vaporizer (steam)	V1247	High Pressure Separator
E1217	Water Condenser (water)	V1249	Overhead Separator
P1037A&B	SRC Feed Circulation Pumps	V1250	Oil Flash Vessel
P1042A&B	Flash Bottoms Pumps	V1251	Flashed Oil Overhead Vessel
P1053A&B	Flash Overhead Pumps	V1252	Water Flash Vessel
P1221A&B	Reactor Feed Pumps	V1253	Water Separator Vessel
P1222	Ebullating Pump		

HTR UNIT FLOWSHEET (Reproduced from reference (14))

APPENDIX 3

NATIONAL COAL BOARD

LIQUID SOLVENT EXTRACTION PROCESS



N.C.B. LIQUID SOLVENT EXTRACTION PROCESS (Reproduced from reference (1))